EFFECT OF DIFFERENT BASE AND DIFFERENT CATALYST IN THE BIOALCOHOL PRODUCTION FROM PALM KERNEL OIL

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JANUARY 2008

Effect of Different Base and Different Catalyst in the Bioalcohol Production from Palm Kernel Oil

By

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Dissertation submitted in partial fulfilment of

The requirements for the

BACHELOR OF ENGINEERING (Hons.)

(CHEMICAL ENGINEERING)

JANUARY 2009

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the referenced and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(KHAIRUL NINA AZREENA BT. MOHD. KHIR)

ACKNOWLEDGEMENT

The writer would like to extend the heartfelt gratitude to the followings from Chemical Engineering Department, UTP who have made the completion of this Final Year Project possible:

1. **Mr. Mohammad Tazli bin Azizan** as the Final Year Project Supervisor and Coordinator for his great advice and consultation throughout the supervision period.
2. **Mr. Surya Abadi**, (PhD. Student) for his guidance in giving ideas to complete the project tasks.

And to all other lecturers and staffs as well as Postgraduate Students of Chemical Engineering Department, UTP, not mentioned above for their help and inspiration they extended.

Not forgetting to the laboratory technologist from UTP that involved in this project especially Mr. Fazli, Mr. Jailani, Mr. Fauzi and Mr. Firdaus, as well as the other laboratory technologist for their aid in carrying out the experiments.

Most especially to my family and friends, especially to those who will be successfully graduating from UTP in August 2009.

And to God, who made all things possible.

Best regards,

Khairul Nina Azreena binti Mohd. Khir

ABSTRACT

The catalyst addition in bioalcohol production from palm based source is driven by the low yield of bioalcohol produced. The ideal objective of this project is to integrate bioalcohol and biodiesel production as to reduce the production cost. However, current bioalcohol and biodiesel that are being produced in a different chemical plant due to its low and uncertainty yield. This project is meant to obtain high yield of bioalcohol. The bioalcohol produced is through partial saponification process of ester. Palm kernel oil is used as raw material due to its abundance in Malaysia. Three experiments have been carried out. The first experiment is to produce bioalcohol without the presence of catalyst and the second experiment is to produce bioalcohol with presence of sodium methoxide as catalyst. Next is the third experiment, whereby calcium methoxide is used as base and catalyst to produce bioalcohol. The bioalcohol products are sent to gas chromatography to be analyzed. As for experiment 1, the concentration of biomethanol 0.0027M while the concentration of bioethanol is 0.026. Besides, the volume of biomethanol is 4.58ml and bioethanol is 4.41ml. In experiment 2, as catalyst 0.05 and 0.1wt% sodium methoxide by weight of oil is added in the experiment, the concentration of biomethanol and bioethanol increase to 0.1247M and 0.0028M respectively. The volume and yield of biomethanol also increase as the amount of catalyst increases. The volume and yield of biomethanol after putting 0.1wt% of sodium methoxide are 47ml and 12% respectively. However, the volume and yield of bioethanol decrease as the amount of catalyst sodium methoxide increases. The volume and yield of bioethanol after putting 0.1wt% sodium methoxide are decrease to 1.09ml and 0.0098% correspondingly. This is due to the methoxide ion that exhibits more biomethanol rather than bioethanol. Thus, the production of biomethanol is favoured. The optimum amount of sodium methoxide is 0.1wt% by weight of oil. Starting from 0.3wt% of sodium methoxide, the reaction formed high yield of soap and less yield of bioalcohol. This had cause the reacted product unable to be distillate using rotary evaporator. As for experiment 3, biomethanol produced also increases as calcium methoxide amount increases, while bioethanol yield is optimized at 0.1wt% of calcium methoxide. The biomethanol rises from calcium methoxide are slower as compared to sodium methoxide usage. Experiment 2 and 3 are known as autocatalytic reaction whereby the product itself is the catalyst for that reaction. In the discussion part, the increment of bioalcohol, the yield of bioalcohol and the bioalcohol amount that should be produced by sodium methoxide and calcium methoxide are discussed. As conclusion, bioalcohol production by using sodium methoxide is favoured over calcium methoxide as it gives high yield and fewer amounts needed. For recommendations, the calcium methoxide concentration needs to be varied to see its effect upon bioalcohol yield. Use of high temperature rotary evaporator is needed to observe the production of propanol and butanol, whereby propanol and butanol will be distillated more at high temperature.

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CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY

This project entitled ***Effect of Catalyst in the Bioalcohol Production from Palm Based Source*** is suggested by Mr. Tazli Azizan, and this one year project will be under his supervision. This project focuses on producing bioalcohol production by using palm kernel oil (PKO). Details of this project will be discussed later in this report.

Currently, petroleum prices have increasing rapidly, caused by the low productivity of fossil fuels and its high demand. The predicted oil price by OPEC is USD$ 50 - 60/barrel until year 2030. However, in November 2007, oil price increases to USD$ 98/barrel. The oil keeps hiking and until June 2008, the oil price is USD$ 143/barrel.

Besides, there are uncertainties of concerning petroleum availability. Fossil fuels which release greenhouse gases especially CO_2, have great contribution to the global warming. Carbon emission started since the industrial revolution, and becomes critical through burning of fossil fuels. Prior to industrial revolution, carbon dioxide concentration on the atmosphere is approximately 280 parts per million (ppm). It increases to 380ppm today, and expected to keep increasing by 2ppm annually. This global warming causes an increment of 1°F, yearly (Biofuel, 2008).

In term of transportation, eventhough engineers have come up with electric and hydrogen cars technologies which are more efficient and environmental friendly, these technologies is not sufficiently mature. In addition, one could not expect people to easily change their cars within few years (Sanquist, 2008). All of the above matters, followed by a growing concern of the environmental have revived more interests in substitute energy in order to replace the fossil fuels.

At present, world is talking about biofuel, a renewable energy which can help in substituting the fossil fuels. Scientists and engineers are struggling conducting research and development of biofuel as to ensure its reliability, at the same time saving the environment by

reducing the greenhouse effect. Research has been directed to explore alternative plant based fuels and plant oils and fats as fuels have bright future (Martini N, 1998). The most common fuel that is being developed and used at present is bioalcohol and biodiesel.

Bioalcohol mainly ethanol have been widely produced to substitute current fossil fuels. Bioalcohol may reduce the emission of greenhouse gases and other pollutants that can lead to global warming. Although the production of bioalcohol may lead to increase of acetaldehyde and formaldehyde, it is believes that these components hardly have impact to the surroundings. Besides, bioalcohol gases create less atmospheric reactivity thus resulting in reduced oxidant (ozone) formation. The absence of sulphur in bioalcohol combined with low emissions of nitrogen oxide from heavy vehicles helps in reduction of pollution (Bioalcohol Fuel Foundation (BAFF)). Currently, bioalcohol can be produced through fermentation, saponification and thermochemical process. Example of raw materials used in fermentation are starch and sugar from grain, or cellulose based products such as wood shavings, forest residues, energy forest and recycled fibre. Brazil is an example of country that produces bioalcohol through fermentation of sugarcane. The bioalcohol produced by them has increases the number of biofuel car used in Brazil, up to 4.6 million biofuel cars. The biofuel cars run by using either petrol or biofuel made from sugarcane (Thomson Financial, 2008).

Biodiesel is an environmentally safe, non toxic and biodegradable fuel. Biodiesel, which is derived from plant oils are widely available from various sources. These raw materials being exploited commercially by the developed countries constitutes the edible fatty oils derived from rapeseed, soybean, palm, sunflower, coconut, linsees etc (W, 1999). Thus, these glycerides are considered as a viable alternative for diesel fuel (Dmytryshyn Sl, 2004).

Plant oils have good heating power and provide exhaust gas with almost no sulphur and aromatic polycyclic compounds. Besides, their burning leads to a complete recyclable carbon dioxide (Stavarache C, 2005). However, their viscosities are much higher than usual diesel fuel. The viscosity can be reduced by a simple chemical process and modifications of the engines.

Palm oils, which will be used in this entire project is the most widely produced tropical oil and known as the common oil used to produce biofuel. By country, the leading producers of palm oil are Malaysia (13 million tons) and Indonesia (10 million tons), and together they have provided about 80% to 90% of the world's palm oil (Biofuel Industries). However, these figures change in year 2006 as Indonesia takes charge as the first leading country of palm oil producer (Indonesia: Palm oil production prospects continue to grow, 2008). Still, as one of the leading producers of palm oil, Malaysia takes an initiative to produce biodiesel from the palm oil.

In Universiti Teknologi PETRONAS (UTP), a novel route was found to produce bioalcohol from oil plant especially those containing high saturated fatty acids (lauric and myristic acids). Palm kernel oil (PKO) is one of palm based sources that has high amount of lauric and myristic acids, approximately 48.2% and 16.2% respectively. Besides PKO, coconut oil has high content of these acids too. These fatty acids help in increasing the yield of bioalcohol, by reacting it with a weak base, e.g. calcium hydroxide, $Ca(OH)_2$ in a partial saponification reaction. Production of methanol and ethanol through this reaction method can be successful in mild temperature range from 60°C to 75°C at atmospheric pressure. This finding was made by team lead by Associate Professor Dr Suzana Yusof, assisted by Mohammad Tazli Azizan.

Concerning on the modest way of producing bioalcohol early, however, this is hindered by the low yield of bioalcohol produced. Thus, it is proposed that the bioalcohol is to be produced with the help of catalyst. Catalyst that is used throughout this project is sodium methoxide, NaOMe.

The bioalcohol produced is the intermediate stage of producing biodiesel. The successful of producing high yield of bioalcohol will lead to the integration of bioalcohol and biodiesel, in such a way that the bioalcohol produced will be used to produce biodiesel. In industry, the biodiesel plant is to be extended to produce bioalcohol as well as biodiesel.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

As mentioned in background of study, UTP has invented a novel route on producing bioalcohol by using PKO or coconut oil as raw materials, with addition of weak base e.g. Ca(OH)2 through partial saponification process. Current research has found difficulties in commercializing this product due to the low yield of bioalcohol produced.

The ideal process of this project is to produce bioalcohol as an intermediate stage of producing biodiesel so that the bioalcohol and biodiesel can be produced in one chemical plant. By integrating the production of bioalcohol and biodiesel, the cost of bioalcohol production can be reduced. However, there is a concern whereby the bioalcohol yield is uncertain and low.

In order for a plant to produce both bioalcohol and biodiesel in one chemical plant, detail plans are needed to ensure that the yield is high and follow the standard given. The process conditions are also important as they helps in determining the overall product yield. As the process is rather complicated, many companies are focusing on producing bioalcohol and biodiesel separately. For companies who are producing biodiesel, they are more willing to buy alcohol from other companies eventhough the price is high.

1.2.2 Significant of the Project

This project signifies the vitality of having bioalcohol as an intermediate stage of producing biodiesel because these biofuel may substitute diesel fuel and thus minimize the reliance on petroleum based source. Besides, this project is important as it helps in finding the most economical feasibility of producing bioalcohol.

Therefore, in this project, catalyst sodium methoxide is used to help in increasing the yield of bioalcohol. Besides, yield of bioalcohol by using calcium methoxide that acted as base and catalyst at the same time is studied.

1.3 OBJECTIVES

As the title of the project implies, the idea of this project is to gain high yield of bioalcohol. To achieve this, many issues need to be addressed. So, the objectives of this project are to:

1. Investigate the effect of catalyst addition on bioalcohol production from PKO.
2. Study the effect of different base which will also be used as catalyst on bioalcohol production from PKO.

1.4 SCOPE OF STUDY

The studies involved in this project are:

1. To conduct partial saponification experiment of producing bioalcohol by reacting PKO with a weak base, calcium hydroxide, in presence of catalyst sodium methoxide. The manipulating variable is the amount of catalyst used. This experiment will follow the methods used by A. Ina Czarina (2008).
2. To conduct partial saponification experiment of producing bioalcohol by reacting PKO with calcium methoxide, which acted as base and catalyst at the same time. The manipulating variable is the amount of calcium methoxide used.
3. To determine the highest yield of bioalcohol that can be obtained by manipulating the amount of catalyst used.

1.5 FEASIBILITY OF PROJECT WITHIN THE SCOPE AND TIME FRAME

This is a one year research project which includes literature review, hypothesis formulation, analytical analysis as well as experimental work. It is planned to find the optimize route of getting high yield of bioalcohol besides investigating the effect of catalyst addition in the bioalcohol production from PKO.

CHAPTER 2
INTRODUCTION TO BIOFUEL

2.1 OVERVIEW OF BIOFUEL

Biofuel, also known as agrofuel, are considered as one of the renewable energy sources. They are derived from recent dead material, which include plants and organic wastes. These biofuel can be found in solid, liquid or gas fuel form. Biofuel are considered as the best alternative to replace fossil fuels which are derived from long dead biological material.

Biofuel, mainly biodiesel and bioalcohol, are used widely in transportation sector. In present, most vehicles used gasoline and diesel fuels as they can provide high power and relatively high dense so that storage is easier. Besides, vehicle engines require fuels that are clean and are in the liquid form. The most important advantage of using liquid as fuel is that they can easily pump and be handled easily.

For other forms of non transportation applications, there are other alternative solid biomass fuels, such as wood. Wood is used as it can easily bear the lower power density of external combustion. Wood has been brought into use since a very long period and is one of the major contributes of global warming (Other alternative fuels).

Biofuel can make a big difference in improving our environment, by providing clean energy services, in such a way that it manage to reduce the carbon emission. Furthermore, it is also believes that biofuel may enhance energy security, improve poverty alleviation and diversify the agricultural and forestry activities.

2.2 GENERATIONS OF BIOFUEL

Generations of biofuel is also known as types of biofuel. The term generation is used to specify the types of biofuel being produced at certain generation, including its development (First Generation Biofuels). There are four generations of biofuel. Details of each generation are discussed below.

2.2.1 First Generation Biofuel

In the first generation of biofuel, fuels are derived from sources like starch, sugar, animal fats and vegetable oil. Biofuel produced namely biodiesel, bioalcohol, biogas, syngas and vegetable oil.

2.2.1.1 Biodiesel

This is the common type of biofuel used in European countries. This type of biofuel is being produced from oils or fats using a process called transesterification. This fuel composition is very similar to the fossil/mineral diesel and is chemically known as fatty acid methyl (or ethyl) ester. This oil is produced after mixing the biomass with methanol (or ethanol) and sodium hydroxide or any other weak base. The chemical reaction thereof produces biodiesel and glycerol. One fraction of glycerol is produced for every 10 fractions of biodiesel (Biofuel, 2008).

Biodiesel is generally used in various engines after mixing up with mineral diesel. Nowadays, many countries manufacturers of the diesel engine ensure that the engine works well even with biodiesel.

2.2.1.2 Bioalcohol

Current technology of producing bioalcohol is by the use of enzymes and micro organisms through the process of fermentation of starches and sugar. Ethanol is the most common type of bioalcohol whereas butanol and propanol are some of the lesser known ones. Ethanol fuel is produced through enzymes digestion, where it is purposely to release sugars from stored starches, fermentation of sugars, distillation and drying. Ethanol fuel can be used

to replace gasoline by mixing bioethanol with gasoline up to certain percentage. By doing this, gasoline with presence of ethanol can increase the octane number. Higher octane number indicates that the engine of a vehicle can be burned more efficiently (Biofuel, 2008).

Biobutanol is also referred to a direct replacement of gasoline because it can be directly used in the various gasoline engines. Butanol is produced using the process of ABE (acetone, butanol, and ethanol) fermentation, and some of the experiments have also proved that butanol is a more energy efficient fuel and can be directly used in various gasoline engines (Other alternative fuels).

2.2.1.3 Biogas

Biogas is normally produced by a process of anaerobic digestion of the organic materials. Biogas can also be produced with the biodegradation of waste materials whereby the waste materials are fed into anaerobic digesters to enhance gas yields. The by product of the process, namely digestate, can be easily used as manure or fertilizers for agricultural use (First Generation Biofuels).

The biogas produced mostly consists of methane or so called as natural gas, which can be easily recovered through the use of mechanical biological treatment systems. Bacteria can also produced methane as they break down cellulosic material, whether in a swamp or bog (CropLife International, 2007). A less clean form of biogas is the landfill gas which is produced by the use of naturally occurring anaerobic digesters, but the main threat is that these gases can be a severe threat if escapes into the atmosphere (First Generation Biofuels).

2.2.1.4 Syngas

Another type of biogas is carbon monoxide rich gas which is made via thermal gasification (CropLife International, 2007). It is also known as syngas. Syngas is produced after the combined process of gasification, combustion and pyrolysis. Biofuel used in this process is converted into carbon monoxide and then into energy by pyrolysis. During the process, very little oxygen is supplied to keep combustion under control. In the last step known as gasification the organic materials are converted into gases like carbon monoxide and hydrogen (Other alternative fuels). The resulting gas Syngas can be used for various

purposes – such as to efficiently combust original biofuel and co-producing biochar (Biofuel, 2008).

2.2.1.5 Vegetable Oil

The oil can be either used for cooking purpose or even as fuel (rarely). The usage of vegetable oil – either to be used as cooking oil for fuel, is determined by the quality of the oil. Oil with good quality is generally used for cooking purpose. Vegetable oil will only be used as fuel in old diesel engines in warm atmosphere. In most countries, vegetable oil is mainly used for the production of biodiesel (Other alternative fuels).

2.2.2 Second Generation Biofuel

Second generation biofuel is produced from non-food crops, by using biomass to liquid technology. These biofuel are believed to increase political and industrial support by avoiding the rising of food prices and reducing land cropped, which are currently caused by the production of first generation biofuel. The second generation biofuel is able to be produced in an environmental friendly way.

Most of second generation biofuel are still in pilot phase due to its complex production process. Examples of biofuel under this generation are biohydrogen, biomethanol, DMF, biohydrogen diesel and wood diesel (Sanquist, 2008).

2.2.3 Third Generation Biofuel

Third generation biofuel, also known as algae or oilgae, is produced from algae (Biofuel, 2008). It is believed to be produced in low cost and high yield, almost 30 times more energy production per acre as compared to the land required by other conventional feedstock to produce biofuel (Minhas, 2008). Furthermore, algae fuel is biodegradable.

In present, researches conducted Alga culture (farming algae) to produce different fuels for making vegetable oil, biodiesel, bioethanol, biomethanol, biobutanol and other biofuel. If the methodology is sustainable than other available biofuels generations, then used

of algae in biodiesel production will be the only viable method to replace the need of gasoline used for automotive today (Minhas, 2008).

2.2.4 Fourth Generation Biofuel

Fourth generation biofuel is focusing on producing fuel directly from carbon dioxide on an industrial scale (Biofuel, 2008). In fourth generation production system, biomass crops are seen as efficient 'carbon capturing' machines that take CO_2 out of the atmosphere and lock it up in their branches, trunks and leaves. The carbon-rich biomass is then converted into fuel and gases by means of second generation techniques. By doing this, the fourth generation biofuel is classified as carbon negative fuel and meant to clean up the atmosphere (Biopact Team, 2007).

2.3 BIOALCOHOL AS TRANSPORTATION FUEL

2.3.1 Biomethanol

According to the President of the United States, the U.S. Environmental Protection Agency, Ford Motor Co., General Motors, Toyota, the California Energy Commission, and other influential organizations and individuals, the transportation fuel of the future in the will be methanol (Daniel Sperling, 1989).

Biomethanol is believed to replace the petroleum as the dominant transportation fuel is because of several explanations:

- Biomethanol can be made from a large number of materials, many of them available in abundance in many countries
- It can be made less expensively than almost all other options
- It burns more cleanly than petroleum fuels
- It is similar to gasoline and diesel fuel whereby it does not require costly changes in motor vehicles and the fuel-distribution system.

Methanol as transportation fuel can be divided into two: neat methanol (100% methanol) and methanol blend. The advantages of neat methanol make the neat methanol

engine to be 30% more efficient as compared to a regular engine (Methanol Conversion Group, 2001). However, the drawback of neat methanol causes the invention of methanol blend (refer Table 1).

Table 1: Advantages and disadvantages of neat methanol (100% methanol) as transportation fuel.

ADVANTAGES	DISADVANTAGES
High octane number than gasoline.	Boiling point 65°C. - Cause problem in cold-starting applications.
High heat of vaporization. - Cools the air in the engine to a larger extent, thus lowering the density and allowing more air in. - More lean fuel mixture and lowering emission of CO.	Low heat of combustion. - Need a tank twice as large, approximately 1.5 to 1.8 times larger in volume compared to gasoline fuel tank. - Need more heat in the intake system to run methanol.
High compression ratio. - Allow more work per unit of fuel.	Corrosion of car parts that are made from lead, magnesium or aluminium.
Low combustion temperature. - Less formation of NO_x.	Saturated methanol-air mixes are explosive at ambient temperatures. - Might cause explosion.
Toxic substances released e.g. benzene and 1,3 – butadiene are eliminated.	

Methanol blends starting at 5% and rising up to 15% have been introduced into transportation sector. These blends only required minor changes for the engine to operate. As for M85 (85% methanol blend), significant modifications need to be made to the engine (Methanol Conversion Group, 2001). Methanol blends may reduce the drawbacks of using neat methanol and at the same time increasing the efficiency of the engine.

As methanol production from biomass or natural gas sources increase over time, higher percentage methanol fuel blends will be introduced eventually up to 100%, taking

advantage of technological development of methanol fueled automobiles. This will enable the global to meet increasingly stringent greenhouse emission reduction goals as well as decreasing the need for what surely will be decreased global oil reserves in the next few decades.

The fuel cell technology has been introduced, and it is believed that it will advance to the point of being a viable alternative to the internal combustion engine, as the methanol to hydrogen, MTH, process is ideal for sustainable transportation needs in the future. The MTH process and fuel cell use has the lowest estimated carbon emissions, zero particulate and NO_x emissions, as well as the highest energy efficiencies (Methanol Conversion Group, 2001).

2.3.2 Bioethanol

Same with neat methanol, neat ethanol has one major drawback – ethanol is more oxygenated, and its combustion in oxygen generates less energy compared with either a pure hydrocarbon or a typical gasoline (refer Table 2).

Table 2: Energy parameters for ethanol, isooctane, gasoline and diesel (Mousdale, 2008).

PARAMETER	ETHANOL	ISOOCTANE	GASOLINE	DIESEL
Density (lb/gal)	6.6	5.8	6.25	7.05
Net heat of combustion, Btu (x 103)/gal	75.7 – 76.0	110.5 – 119.1	109.0 – 119.0	128.7 - 130
Octane no. (mean of research and motor octane no.)	104.5		90.5	
Octane no. (research octane no.)	106	100		

The higher density of ethanol does not mitigate this problem. This is because the liquid volumes are dispensed volumetrically and higher weights in fuel tanks represent higher loads in moving vehicles. Therefore, a gallon of ethanol only represents 70% of the energy capacity of a gallon of gasoline.

Besides, eventhough ethanol has a higher octane number which leads to higher energy efficiencies, and also generated an increase volume of combustion products (gases) per energy unit burned, the net heat of combustion of ethanol is still low, approximately 58 – 59% of the latter (Mousdale, 2008). Thus, ethanol blends are introduced as a more conservation option.

Low-ethanol additions to standard gasoline e.g. E10 (90% gasoline and 10% ethanol) requires no modifications to standard gasoline-burning vehicles. United States of America (U.S) is currently blend this typical ethanol blends. However, Brazil employs 22% blends of ethanol in all gasoline used (Wyman, 1996). This improvement can largely compensate for the fact that ethanol has about two-thirds of the volumetric energy content of gasoline, and a vehicle should be able to travel about 75 – 80% of the distance on a given volume of ethanol as on the same volume of gasoline.

Many flexible fuel vehicles (FFV) or so called as the "flexi fuel" that can run on any mixture of gasoline and ethanol have been introduced. Among the first motor company to invent this is Ford (Mousdale, 2008). This is followed by several other motor companies such as Citroen, Skoda Auto, Audi, Renault and Mitsubishi (Bioalcohol Fuel Foundation (BAFF)).

Figure 1 below shows the quantity of fuel ethanol production in the world from year 1975 until 2005, sorted by region. The figure also predicts the quantity of fuel ethanol production in year 2010. From the figure, it shows that the fuel ethanol production in Brazil and US are the highest. This is followed by Australia and any other countries.

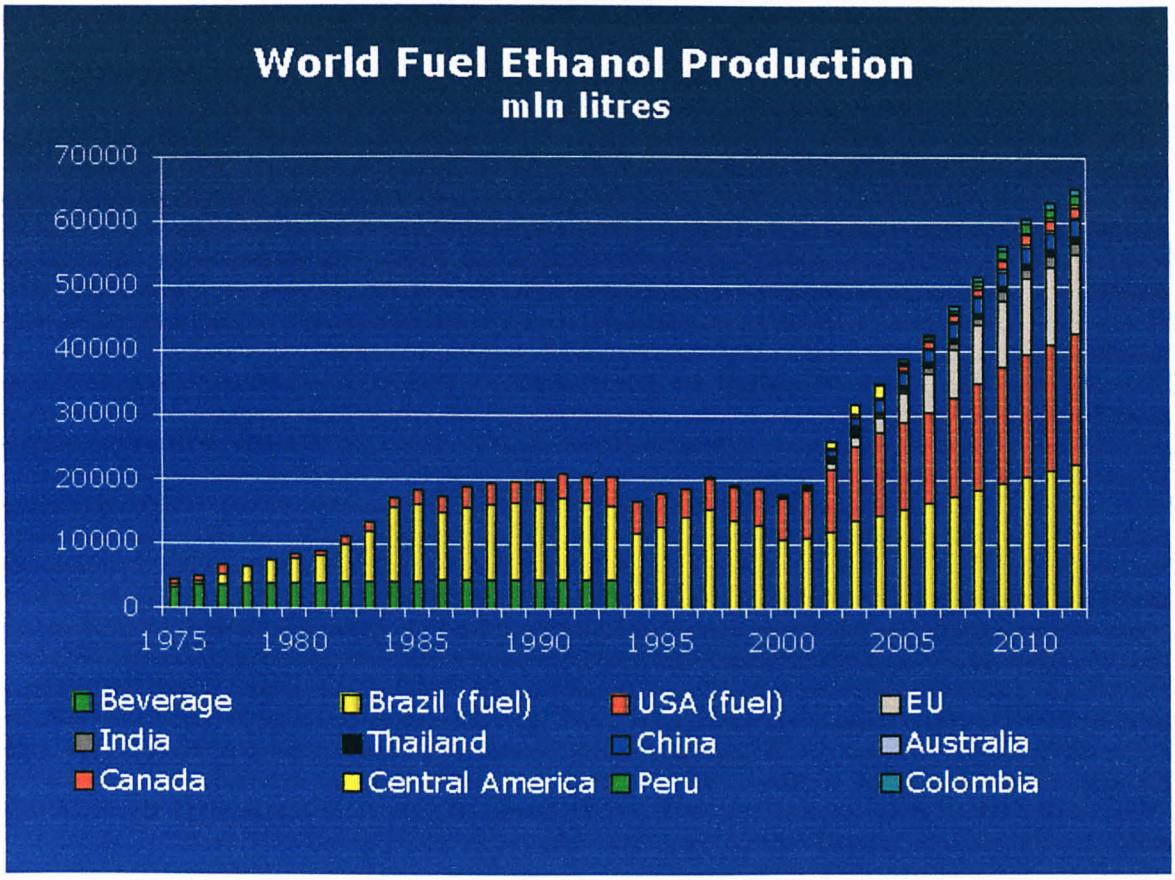


Figure 1: Fuel ethanol production, 2000 and 2005 (billion litres/year). *(Berg, 2004)*

2.4 BIOALCOHOL WORLD DEMAND

As mentioned before, bioalcohol has been produced widely especially in Brazil. In 2003, Brazilian automobile producers introduced truly FFVs with engine capable of being powered by gasoline, 93% aqueous ethanol, or by a blend of gasoline and anhydrous ethanol. In 2004, flex-fuel cars sold in Brazil were 16% of the total market, but during 2005, sales of FFVs overtook those of conventional gasoline vehicles. Domestic demand for ethanol-containing fuels became so great that the ethanol percentage was reduced from 25% to 20% in March 2006. This occurred despite the increased production of anhydrous ethanol for blending. Brazil had evolved a competitive, consumer led dual-fuel economy where motorists made their rational choices based on the relative prices of gasoline, ethanol and blends. They observed that consumers tend to buy ethanol only when pump price is 30% below gasoline blends (Mousdale, 2008).

Up until August 2008, Brazil has produced 4.6 million of biofuel cars, which run either using petrol or bioalcohol made from sugarcane. In 2007, Brazil sold 2 million of biofuel cars which is equivalent to 85.6% of the overall cars sold in Brazil. It is expected that on 2013, half of Brazilian cars will be biofuel, quadrupling the current number. The production of flex fuel cars have led to the investment of USD$ 4.25 billion in sugar and ethanol production, as well as the creation of 1.18 million jobs up to year 2006 (Thomson Financial, 2008).

As for the exports of ethanol and sugar, ethanol became a major exported commodity from Brazil between 1998 and 2005. Exports of ethanol increased by more than 17-fold, whereas sugar increased by less than twofold.

Several countries have demanded for fuel ethanol, mainly Japan, US and Europe. Figure 4 below shows the figures of fuel ethanol import by these countries from year 2005 and the predicted figures until year 2012. The figure shows that Japan will be the major contributor towards the fuel ethanol imports, followed by US, Europe and other countries.

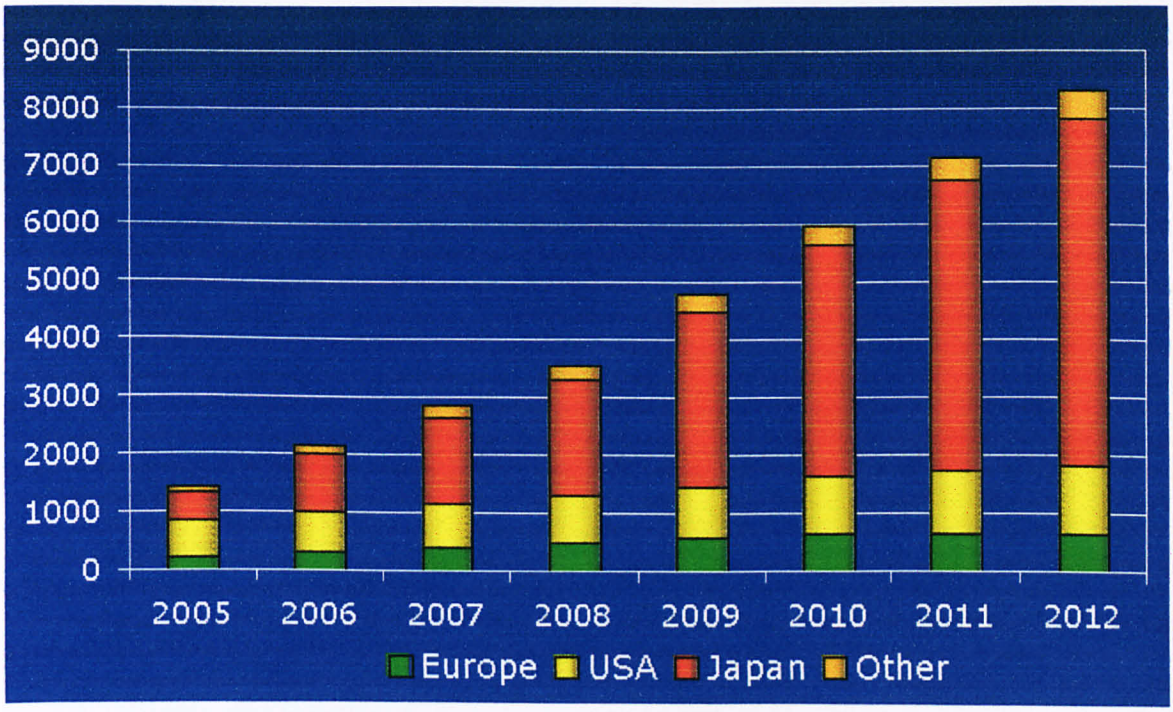


Figure 4: World fuel ethanol imports (million litres). *(Berg, 2004)*

The world demand for fuel methanol is low as compared to fuel ethanol. The demand for fuel methanol in 2005 is only about 4% out of other methanol usage, with an average growth of 5% until 2010 (refer Figure 5 and 6).

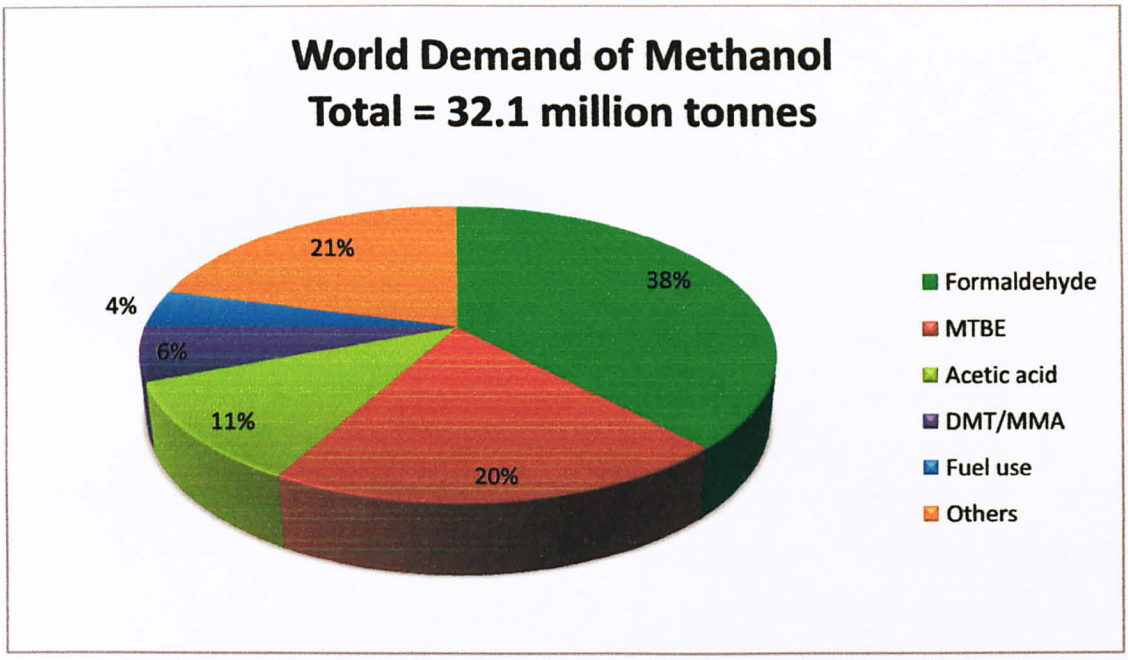


Figure 5: World demand of methanol, year 2005. *(Prakash, 2008)*

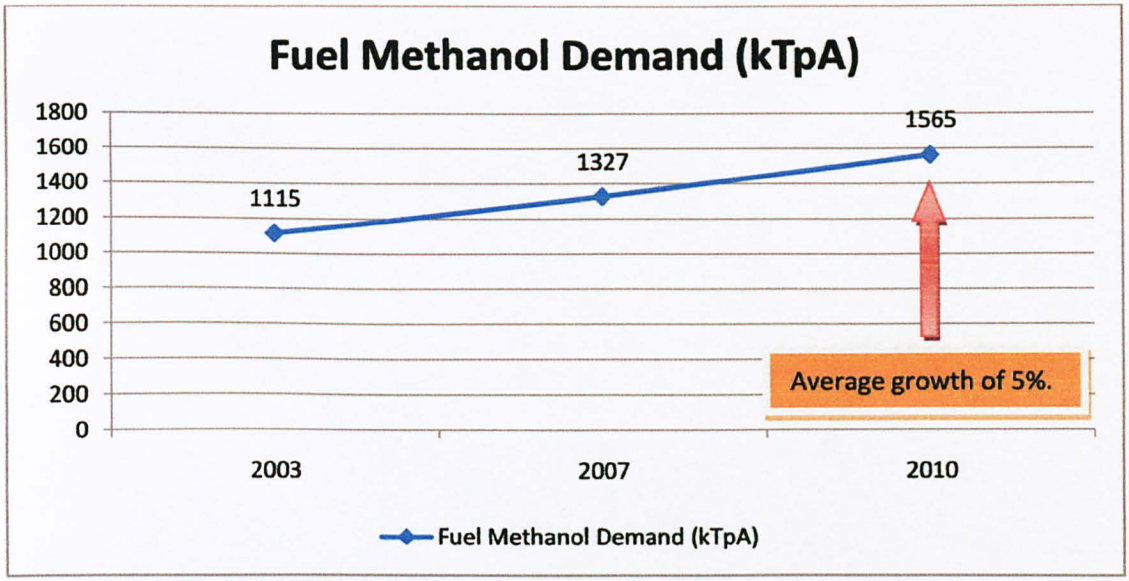


Figure 6: Predicted growth of fuel methanol in 2010. *(Metcall, 2006)*

2.5 INTEGRATION OF BIOALCOHOL AND BIODIESEL

As mentioned in Chapter 1, current technology of producing biodiesel and bioalcohol separately is due to the low yield of bioalcohol. Thus, many companies or countries prefer to import or buy bioalcohol from other places. For certain countries that are known for their high bioalcohol production, it is such a waste to produce the bioalcohol and biodiesel separately. Besides, the production cost of producing bioalcohol and biodiesel separately is high. These situations lead to the integration of these two biofuel in such a way that these two biofuel are to be produced in one chemical plant. The integration of bioalcohol and biodiesel using a single source of biomass as a raw material may allow the intensification of liquid biofuel production offering attractive alternatives for lowering production costs. In addition, the abundance of raw materials for the production of these biofuel will help in lowering the production cost.

Current technology proposed by L.F. Gutiérrez et. al. (2007) is that if the integration of lines for processing palm oil and lignocellulosic biomass is considered, the synthesis of an integrated technological scheme for biodiesel production is feasible. In this case, the purchase of bioalcohol is not involved, but the production of ethanol inside the same process is contemplated.

The idea is that the lignocellulosic residues obtained during the extraction of crude palm oil (CPO) are utilized for ethanol production. High amount of lignocellulosic residues can be obtained from the empty fruit bunch (EFB) and palm press fiber (PPF). Details of the composition are as below:

Table 3: Average composition of two solid residues, EFB and PPF obtained during palm oil extraction. *(L.F. Gutiérrez, 2007)*

Component	Content, % (w/w)	
	EFB	PPF
Cellulose	15.47	24.00
Hemicellulose	11.73	14.40
Lignin	7.14	12.60
Ash	0.67	3.00
Oil	-	3.48
Others	-	2.52
Moisture	65.00	40.00

Source: Abdul Aziz *et al.* (2002a; 2002b), Wan Zahari and Alimon (2004).

The oil extracted from FFB is used as feedstock for biodiesel production, taking into account an integrated process of extractive reaction using ethyl alcohol produced from the lignocellulosic residues for the transesterification reaction, and with presence of base catalyst, potassium hydroxide, KOH.

The integration of bioethanol and biodiesel are achieved by extraction reaction, where it is a combination of chemical reaction and liquid-liquid extraction in the same unit. By doing this, there will be increased in selectivity, conversion, productivity and purity of biodiesel. Two liquid phases are formed during the reaction, and these phases are separated in the same reactor-extractor by an adequate control of agitation. Biodiesel enriched liquid is continuously removed from the reactor-extractor and sent to a flash unit where ethanol is recovered and recycled back to the reactor-extractor. Thus, high purity of biodiesel is obtained. Besides, glycerol-enriched liquid from the bottom of reactor-extractor is sent to distillation column to separate glycerol and ethanol. High purity of glycerol is obtained and high content of ethanol is removed as distillate (see Figure 7).

In order to find out the energy and material balances of the process, simulation is carried out. The simulation results are shown in Table 4 below. The proposed scheme allows the production of high-purity biodiesel that is verified by the elevated level of ethyl oleat in the corresponding stream. The conversion of triolein (triglyceride) reaches 99.9%, and the purity of ethyl oleat is 97.84%. Compared to normal biodiesel synthesis, the percentage yield of biodiesel is 94%. This integrated configuration makes possible the production of the necessary amount of anhydrous ethanol required by the conversion of the extracted crude oil into biodiesel from 122 tonnes/day of FFB. The ethanol required by the process is obtained from the lignocellulosic residues generated during the extraction of palm oil. In addition, a remaining amount of anhydrous ethanol for sale as fuel ethanol is produced (78.0 kg/h).

From this proposed project, the energy cost of producing biodiesel is reduced to 21.3%. Biodiesel production from oil palm by a configuration that utilizes ethanol produced from the solid residues of the same palm, offers such degree of integration that makes possible the decrease of energy costs compared to the autonomous production of biodiesel and bioethanol. This option is very attractive taking into account not only the energy consumption, but also the decrease of the solid wastes generated during the processing of oil palm.

As to compare with this project, the difference is that the ideal of this project is to produce bioalcohol from palm kernel oil through partial saponification. This is because the mild temperature and pressure may cut down the production cost to be lower than the method proposed here.

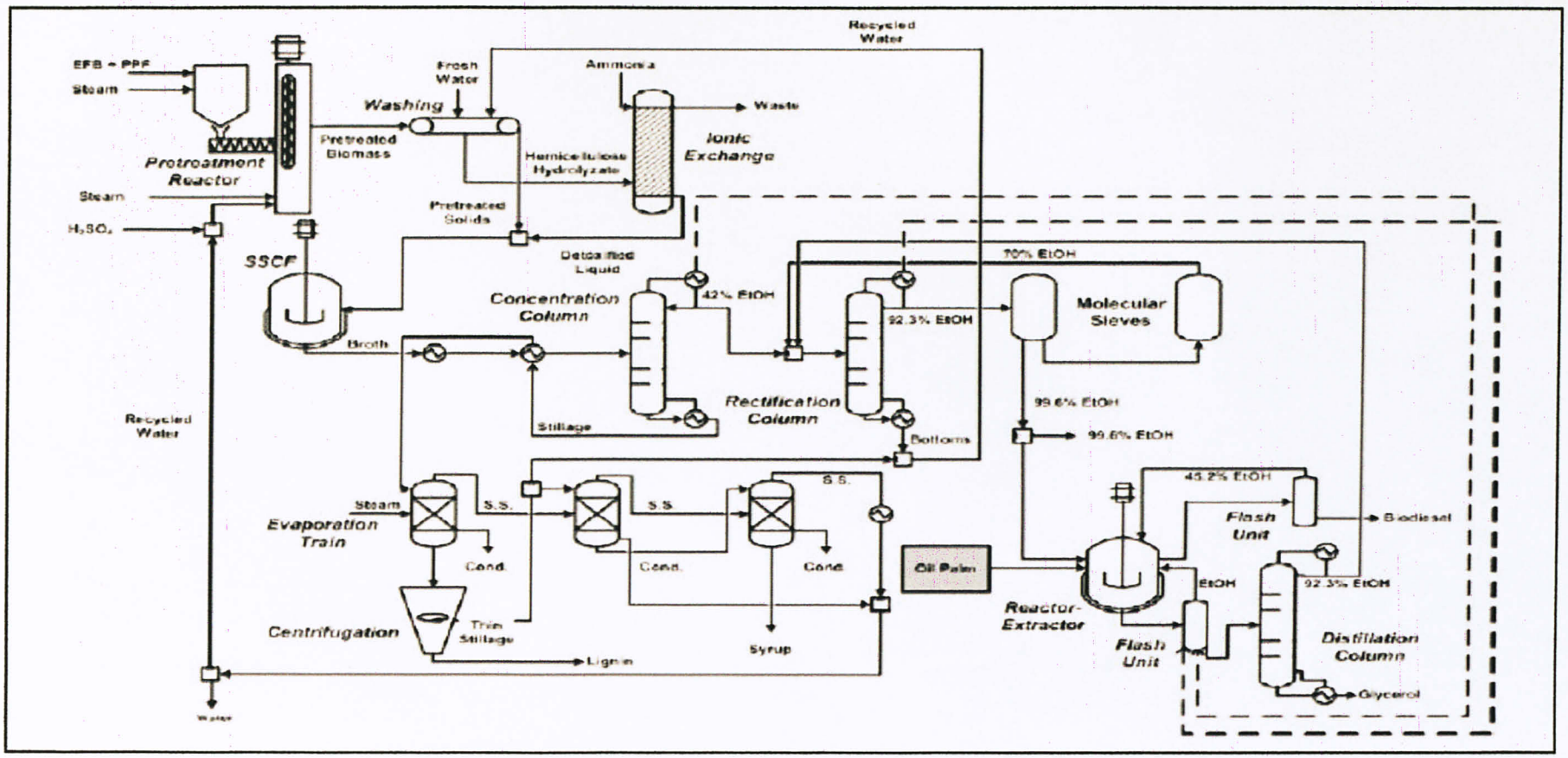


Figure 7: Integrated technological configuration of the combined production of biodiesel and bioethanol. *(L.F. Gutiérrez, 2007)*

Table 4: Simulation results of the integrated scheme for biodiesel production *(L.F. Gutiérrez, 2007)*.

Streams	Lignocell. Biomass	Broth	Recycled water for washing	Rectific. Column distillate	BioEtOH	Biodiesel	Glycerol
T, °C	20	30	77.4	93.4	25	52.4	254.7
p, bar	1.013	1.013	1.793	1.793	1	0.2	0.4
Mass flow, kg/h	1913.1	4185	667.3	347.1	260.1	959.4	95.7
Cellulose, %	18.38	1.52	0.04	-	-	-	-
Hemicellulose, %	12.52	1.31	0.03	-	-	-	-
Lignin, %	9.05	3.72	0.09	-	-	-	-
Glucose, %	-	0.56	0.5	-	-	-	-
Xylose, %	-	0.67	0.89	-	-	-	-
Water, %	56.84	80.47	97.78	7.66	0.41	0.01	-
Triolein, %	-	-	-	-	-	0.44	-
Diolein, %	-	-	-	-	-	0.34	1.88
Monoolein, %	-	-	-	-	-	0.03	2.1
Ethanol, %	-	5.59	0.01	92.34	99.57	1.32	0.03
Ethyl oleat, %	-	-	0.01	-	-	97.84	-
Glycerol, %	-	-	0.02	-	-	0.02	95.94

2.6 SUSTAINABILITY OF BIOALCOHOL

2.6.1 Economical

In term of raw materials, there are many types of raw materials that can be used to produce bioalcohol. These raw materials are cheaper and abundance. Besides, bioalcohol produced by these raw materials are cheaper as compared to the current price of gasoline. Cellulose based ethanol and sugarcane based ethanol are examples of bioalcohol that have low price value as compared to the current gasoline.

As for this project, the raw material which is palm kernel oil is abundance as Malaysia is one of the largest producers of palm oil. In addition, the base used which is a weak base is also cheap. With the help of mild operating conditions – low temperature and pressure, this project is more economical.

The bioalcohol production is also sufficient to provide more than two-third of current global demand for transport energy (Carstedt, 2008).

2.6.2 Social

In term of social, production of bioalcohol through biorefinery has helped the local people to grab a job opportunity. For an example, the sugar/ethanol sector in Brazil employed 3.6 million people, directly and indirectly. The bioalcohol sector encourages commitment and collaboration among workers in the same industry. On top of that, the sugar/ethanol sector in Brazil contribute about 3.5% of the gross national product and $1.5 billion in taxation revenues, have encourage the cooperation to the people within the country as it helps to improve the economical development of the country.

2.6.2 Environmental

Bioalcohol productions have large contributions toward environment. One of the major contributions is the reduction of CO_2 emission. For examples:

- Cellulose based ethanol and synthesis gas has the potential to reduce 90-100% of fossil CO_2 "Well-to-Wheel".
- Sugarcane based ethanol provides already 85% net CO_2 reduction.

Example of proven CO_2 reduction is in London, whereby the CO_2 released by bus is reduced from 20% to 2.5% per gram/passenger-km (see Figure 8).

As for this project, the less inventories needed, the less risk associated. Besides, the mild operating temperature means that the process is less hazardous and less number of chemicals made it easy for waste management. Less cost for waste management and thus better life cycle analysis.

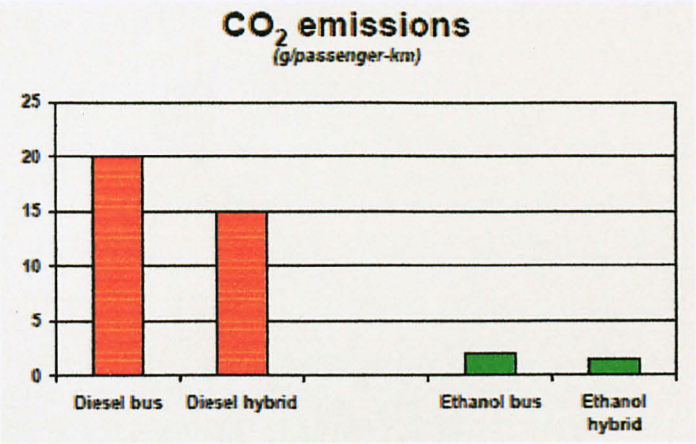


Figure 8: Comparison between diesel and ethanol's CO_2 emission by public bus in London.

CHAPTER 3
LITERATURE REVIEW – BIOALCOHOL PRODUCTION PROCESS ROUTES

3.1 BIOCHEMICAL - FERMENTATION

Raw materials for this process are lignocellulosic biomass such as agricultural residues (e.g. corn stover and wheat straw), forestry wastes, wastepaper, yard waste and other components abundant in municipal solid waste. Typically about 30 – 50% of the lignocellulosic biomass is composed of cellulose, a long chain of glucose sugar molecule joined together in a crystalline structure. Another 20 – 30% is made up of hemicelluloses – a long chain of sugar molecules that made up of a mixture of sugars, often dominated by the five carbon sugar, xylose (Wyman, 1996).

Together, cellulose and hemicelluloses compose about 65 – 75% of the overall lignocellulosic biomass composition. These materials are then broken down to form their component sugars for fermentation into bioalcohol, much as for starch conversion to sugars. However, it is easier to derive sugar from corn or sugar cane. Cellulose and hemicelluloses are broken down to their components sugars by the used of acid or enzymatic based approaches.

$$6CO_2 + 6H_2O + \text{light} \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

Then, these sugars are fermented to bioalcohol by adding yeasts, bacteria, or other suitable organisms, and the ethanol is recovered by distillation or with other separation technologies for use as fuel. The outline of fermentation process is as in Figure 9 below.

$$\textbf{Fermentation: } C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2 + \text{heat}$$

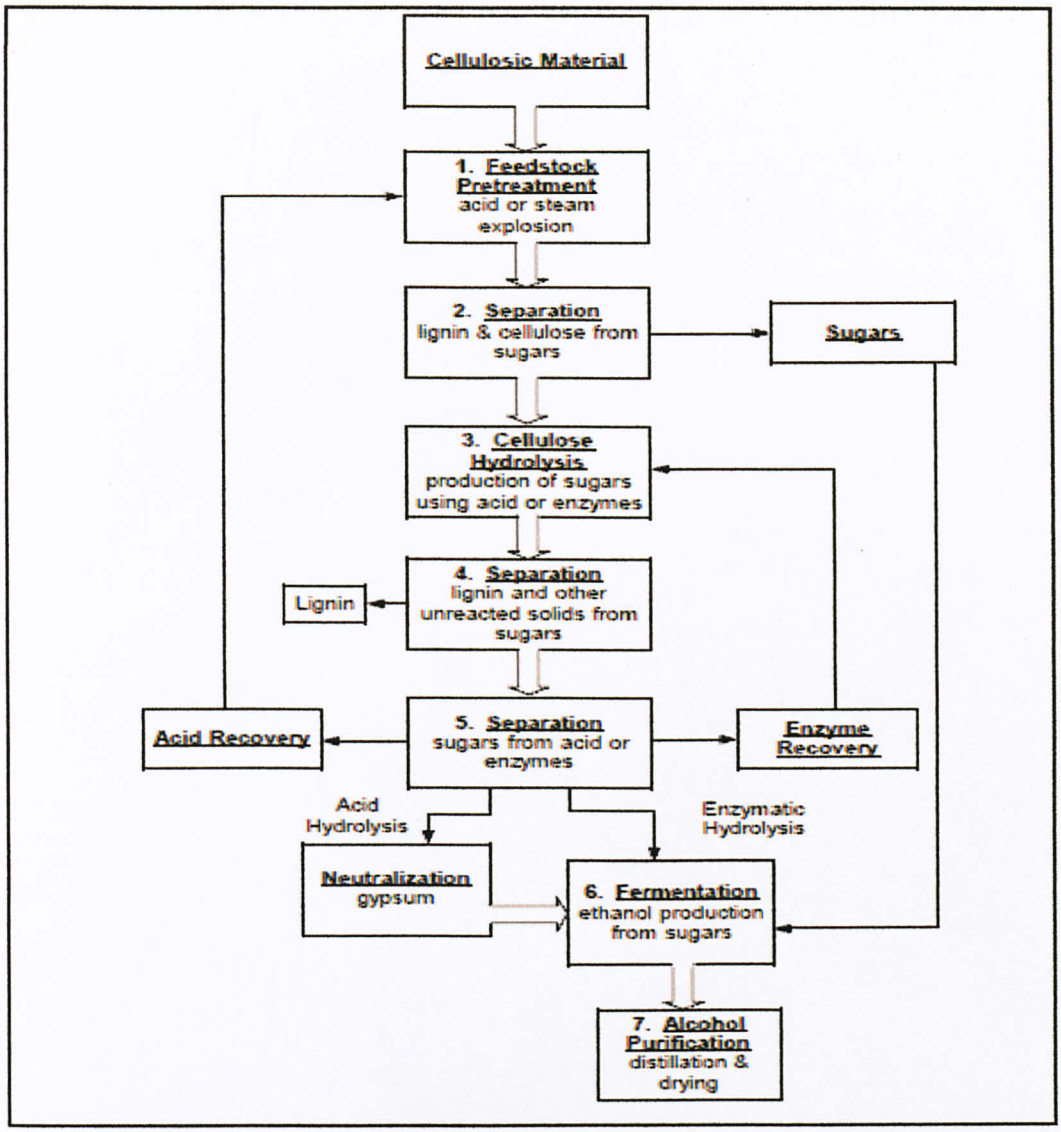


Figure 9: Biochemical process of producing bioalcohol through fermentation. *(Dennis Schuetzle)*

3.2 THERMOCHEMICAL PROCESS

The thermochemical conversion processes that incorporate air or oxygen typically produce syngas that has a low BTU value (<300 BTU/cubic ft.) and potentially high concentrations of tars, particulate and other contaminants. Although these types of technologies have been used for over seventy years for the large-scale production (> $1 billion plants) of electricity, fuels and chemicals from fossil-based feedstocks, these technologies appear less viable for alcohol fuel production, and for smaller-scale production plants (200-1,000 BTD/day) (Dennis Schuetzle). Thus, thermochemical process by

employing pyrolysis/steam reforming processes (no oxygen or air); appear to be the most promising thermochemical approach for producing alcohol fuels from biomass (refer Figure 10).

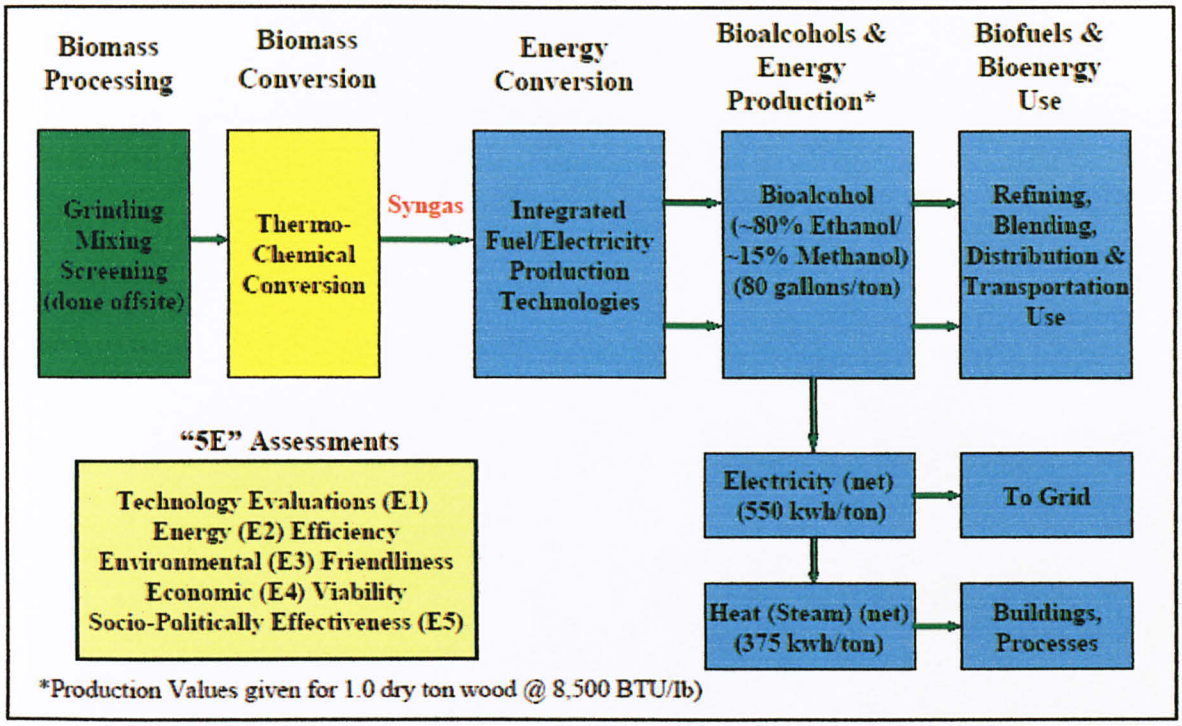


Figure 10: General thermochemical process outline of producing bioalcohol. *(Schuetzle, 2007)*

3.3 INTEGRATED THERMOCHEMICAL AND BIOCHEMICAL PROCESSES

Large-scale biochemical conversion plants appear to be most viable when significant quantities of biomass are available at feedstock costs. A particularly promising application is to co-locate these plants with large, traditional corn-to-ethanol or sugarcane-to-ethanol production plants. Thermochemical processes can also be integrated with biochemical processes to supply electricity, heat (steam), cooling and the production of additional ethanol from waste materials. These integrated approaches are expected to increase plant energy efficiency, reduce emissions and increase economic benefits.

3.4 PARTIAL SAPONIFICATION

Saponification is a hydrolysis process of an ester in producing alcohol and salt of carboxylic acid under the basic condition as it is a reaction of a strong metallic alkali (base) with an animal fat or vegetable oil to form two products – soap and glycerine. Water is present but will not involve in the chemical reaction (Shahidi, Bailey's Industrial Oil & Fat Products Volume 6, 2005).

The saponification reaction can be done in two ways – from free fatty acids and from ester. The second option which is the saponification reaction from ester is chosen as alcohol can be produced from ester with base. In this project, the ester is from palm kernel oil.

PKO + Base → Bioalcohol + Carboxylic salt

CHAPTER 4
RAW MATERIALS

4.1 PALM OIL

This project is only emphasized on producing bioalcohol by using palm based source. Palm oil bioalcohol is an environmental-friendly, renewable energy source that could also produce cost savings for taxpayers and private businesses and is produced from palm trees (Biofuel Industries).

Palm trees are 'unisexual' such that they have male and female flowers within the tree. The female flowers bears fruit known as "fresh fruit bunches", also known as FFB (refer Figure 11). Each palm tree is capable of bearing about 10 to 12 bunches per year. Each FFB averages 1000 to 3000 fruits with weights varying between 40 to 70 pounds (Biofuel Industries).

Figure 11: Fresh fruit bunches (Malaysian Palm Oil Council).

There are two main palm based source products, namely crude palm oil (CPO) and palm kernel oil (PKO). Palm oil is obtained from the mesocarp (the fleshly portion of the fruit wall) and depending on the variety and age of the palm (refer Figure 12). It is orange

liquid and semi solid at room temperature, melting to a clear red-orange liquid on slight heating (refer Figure 13). The CPO to bunch ratio is about 25 to 28 percent.

Palm kernel oil is extracted from palm fruit seed, crushing of palm kernel (refer Figure 12). It is light yellow liquid at room temperature (see Figure 13) (Palmbase Group, 2004).

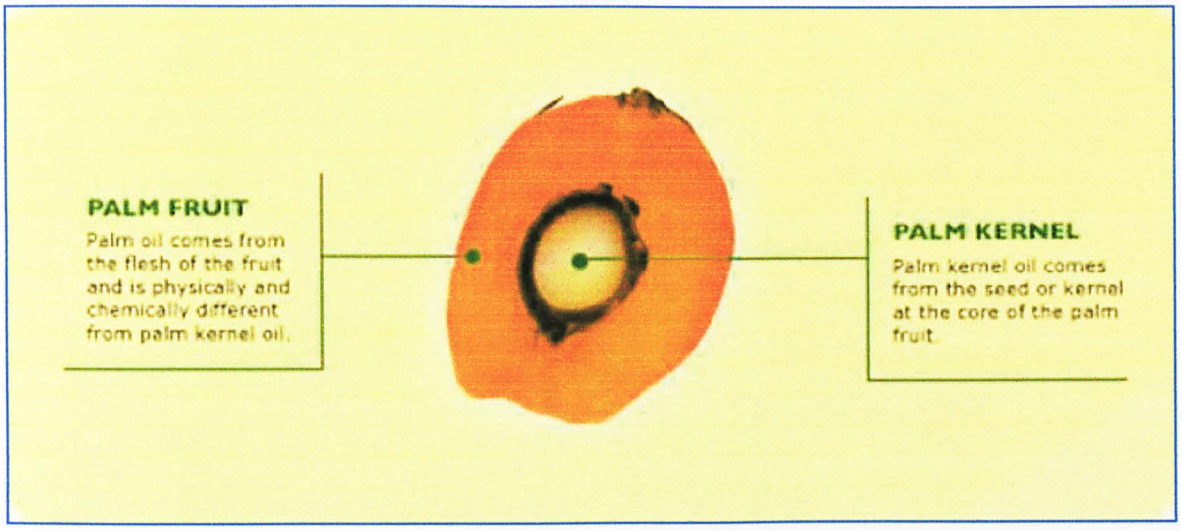


Figure 12: Crude Palm Oil and Palm Kernel Oil (PALM OLIVE).

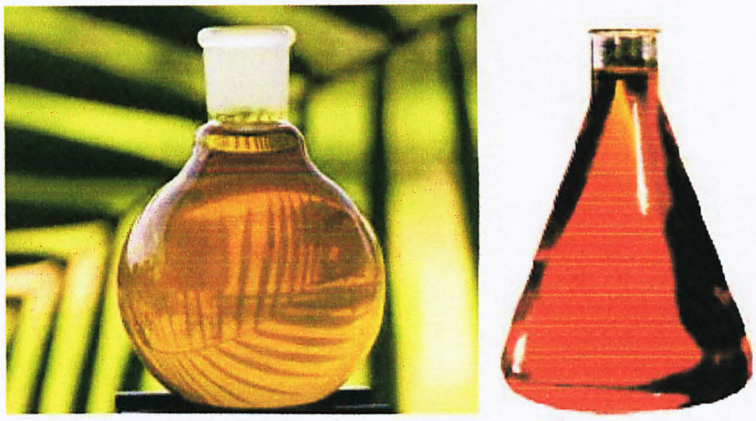


Figure 13: Difference in colour between palm kernel oil and crude palm oil (Malaysian Palm Oil Council).

4.1.1 Performance of Palm Oil Biofuel

Palm oil based biofuel, mainly biodiesel is believed to have high chances of survival under certain conditions compared with biodiesel based on canola oil or rapeseed. 1.2 tonnes of fossil fuel is needed to produce one tonne of canola oil based biodiesel. Unlike palm oil based biodiesel, it does not require that much of fossil energy due to palm based biomass which is used in the heating boiler system that produces biodiesel (Palm Oil Truth Foundation).

Palm oil based biodiesel has been tested as a substitute for diesel in transportations. The results gained shows that cold starting is easy and engines run smoothly with less smoke and reduced content of carbon particles in the exhaust fumes (American Palm Oil Council).

4.1.2 Palm Oil Producers and Demand

Palm oil with an estimated global (annual) production of 25 – 27 million tons is the second most produced oil in the world. By country, the leading producers of palm oil are Malaysia (13 million tons) and Indonesia (10 million tons), and together they have provided about 80 – 90% of the world's palm oil (see Figure 14) (Indonesia: Palm oil production prospects continue to grow, 2008).

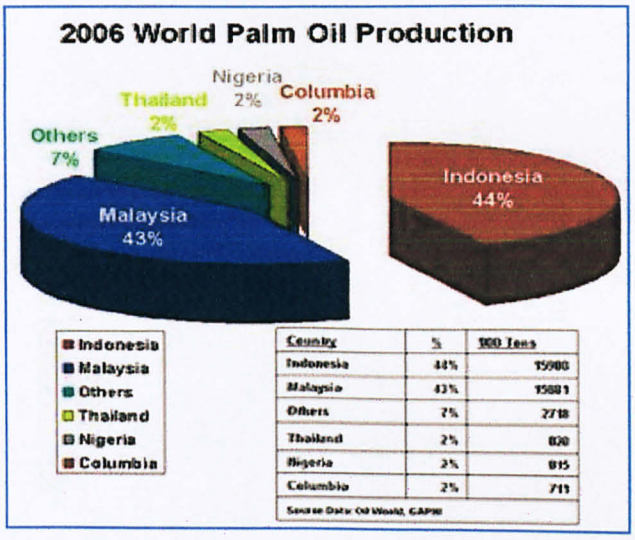


Figure 14: 2006 world palm oil productions. Malaysia and Indonesia account for 87% of world production (Indonesia: Palm oil production prospects continue to grow, 2008).

Approximately 80% (21 – 23 million tons) of the global production of palm oil is exported to other countries. Malaysia exports about 12 million tons annually and Indonesia exports about 7 million tons annually to the major importers of palm oil, which include India, China and European Union (EU). However, in year 2007, Indonesia takes charge as the first palm oil producer. Indonesia produced 18.3 million metric tons of palm oil in August 2007 (refer Figure 15).

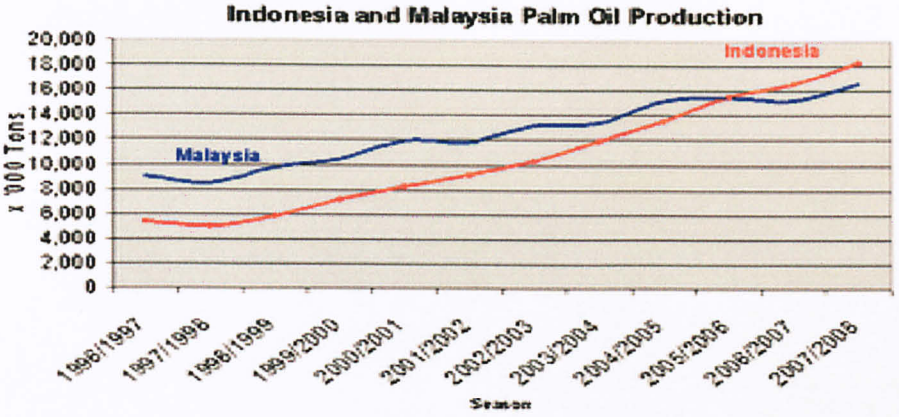


Figure 15: Indonesia and Malaysia Palm Oil Production Year 1996 – 2008 (Indonesia: Palm oil production prospects continue to grow, 2008).

European countries have promoted the use of palm oil by injecting hundreds of million of dollars into national subsidies towards biodiesel. Europe is now a leading importer of palm oil. Through the subsidizing of biofuel, European governments have accelerated the demand for palm oil in Europe and as a consequence have accelerated the conversion of large areas of rainforest in South East Asia. Palm oil plantations are often expanded by clearing existing forest land and draining peat swamps. Many economists predict it will be the leading internationally traded edible oil by the year 2012.

Currently, Malaysia is emerging as one of the leading biofuel producers with 91 plants approved and a handful now in operation, all based on palm oil. On December 2007, the first biodiesel plant in Malaysia is opened with annual capacity of 100 000 tons. Besides, this biodiesel plant also producing by-products in the form of 4000 tons of palm fatty acid distillate and 12000 tons of pharmaceutical grade glycerine. Malaysia is targeted to produce

800 000 tons of biodiesel in year 2010. Palm oil price on December 2007 is claimed to be RM 2550/metric ton (PalmOil.com, 2008).

4.2 TRIGLYCERIDE

Palm oil is made up of triglyceride molecules, the smallest particle of a pure chemical substance that still retains its chemical composition and properties. Chemical analysis reveals that the triglyceride molecule is made up of carbon, hydrogen and oxygen atoms, which can be presented in a structural formula. This is one triglyceride structure prevalent in palm oil (refer Figure 16).

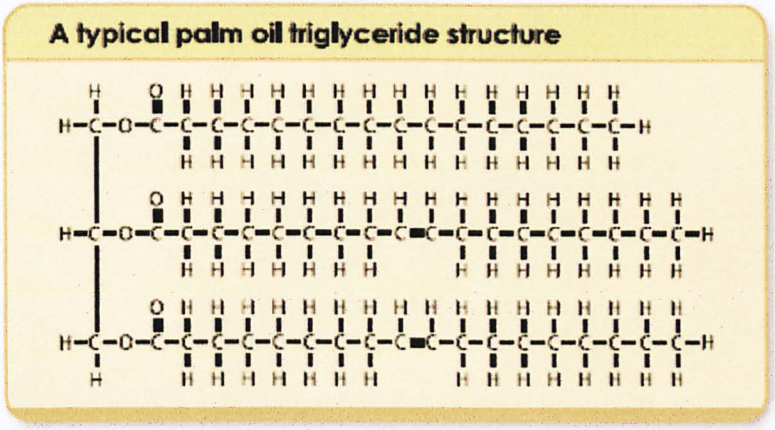


Figure 16: Palm oil triglyceride structure (Malaysian Palm Oil Council).

At first glance, the triglyceride structure looks rather intimidating. The prefix 'tri', gives us a clue that there are 'three' in the structure. A closer look shows that it is shaped like an 'E'. It has three long horizontal arms called fatty acids and each of them, is attached to the same vertical 'frame' called glycerol. The arrangement puts the triglyceride structure in a more manageable form (refer Figure 17).

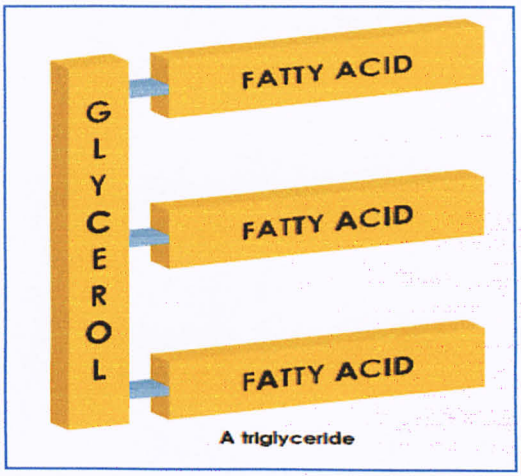


Figure 17: Manageable structure of triglyceride.

4.3 FATTY ACIDS

There are nine main fatty acids in palm oil – these are named according to the number of carbon atoms present in the acid. The behaviour of palm oil and its physical characteristics are strongly influenced by the chemistry of these individual fatty acids and the position they occupy in the triglyceride structure. Nine types of fatty acids in palm oil are shown in Table 5 below. Fatty acids contained in palm kernel oil are shown in Table 6. The fatty acids in palm kernel oil are slightly the same as fatty acids contained in coconut oil.

Table 5: Fatty acid compositions of Malaysian Palm Oil (Shahidi, 2005).

Fatty Acid		% of Total	
Chain Length	Name	Mean	Range
Saturated			
C12:0	Lauric	0.23	0.1 – 1.0
C14:0	Myristic	1.09	0.9 – 1.5
C16:0	Palmitic	44.02	41.8 – 46.8
C18:0	Stearic	4.54	4.2 – 5.1
C20:0	Arochidic	0.38	0.2 – 0.7
Unsaturated			
C16:1	Palmitoleic	0.12	0.1 – 0.3
C18:1	Oleic	39.15	37.3 – 40.8
C18:2	Linoleic	10.12	9.1 – 11.0
C18:3	Linolenic	0.37	0 – 0.6

Table 6: Fatty acid compositions in palm kernel oil (Pantzaris).

Fatty Acid	Composition (Mean Value)
C6	0.3
C8	4.2
C10	3.7
C12	48.7
C14	15.6
C16	7.5
C18	1.8
C18:1	14.8
C18:2	2.6

Fatty acids are categorised into two distinct groups – saturated and unsaturated. The unsaturated is further divided into monounsaturated and polyunsaturated. Saturated fatty acids do not contain any double bonds or other functional groups along the chain. The term saturated refers to hydrogen, in such a way that all carbons (except carboxylic acid group) contain as much hydrogen as possible. The saturated fatty acids form straight chain, and as a result can be packed together tightly (refer Figure 18).

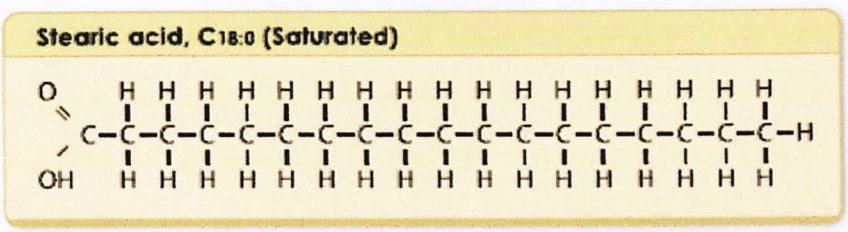


Figure 18: Example of saturated fatty acids, stearic acid (Malaysian Palm Oil Council).

As for unsaturated fatty acids, they are similar, except one or more alkenyl functional group exist along the chain, with each alkene substituting a single bonded part of the chain with a double bond portion. The two next carbon atoms in the chain that are bound to either side of the double bond can occur in cis or trans configuration (refer Figure 19).

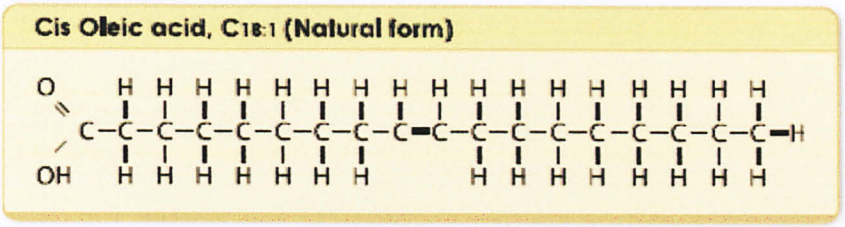


Figure 19: Example of unsaturated fatty acids, cis oleic acid (Malaysian Palm Oil Council).

4.3.1 Free Fatty Acids (FFA)

Palm fruit contains an active enzyme called lipase. The minute the fruit is bruised, the enzyme present is released. This attacks the triglyceride and breaks up the fatty acid into free fatty acid. The irreversible process, called hydrolysis, is a fast reaction and it is done in the presence of water (refer Figure 20). The enzyme, however, can be inactivated by temperature above 55°C.

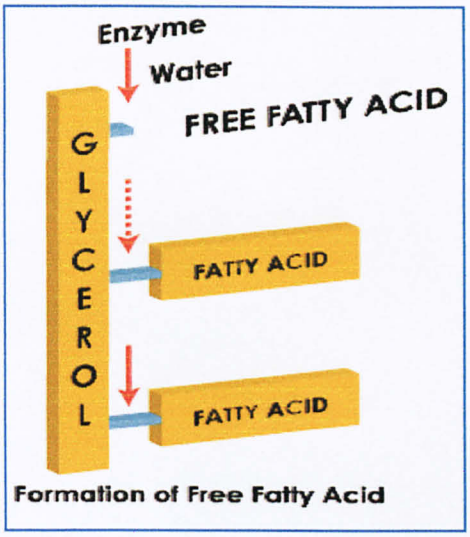


Figure 20: Formation of free fatty acids, with presence of water (Malaysian Palm Oil Council).

The aim in extracting oil from palm fruits must therefore to be minimizing hydrolysis. This is because as fruits ripen, there will also be a corresponding increase in FFA. The change is not as rapid as when the fruits are damaged. The other period where FFA can increase is during storage due to microbial action in the presence of water.

The more the palm fruits are handled, the higher the damage. The higher the content of FFA, the poorer the oil quality since FFA will have to be removed during refining.

4.4 CATALYST USED

In this project, the catalyst used is sodium methoxide (NaOMe). This is because NaOMe exhibits faster and yield more ester at same concentration as compared to sodium hydroxide (NaOH). Emulsion was found to form during the purification of esters from experiment using NaOH. This causes the losses in the product and thus lowering the yield of ester produced. Besides, NaOMe is much easier to handle as it is available in solution, unlike NaOH that requires to be diluted (Cheng, 2004).

CHAPTER 5
PARAMETER USED

5.1 MANIPULATING VARIABLE

Parameters changed in this project were the amount of catalyst, NaOMe and the amount of calcium methoxide, which acted as base and catalyst at the same time. Both of the chemicals amount were in term of weight percent by weight of oil. Details of the variation amount will be discussed later in Chapter 7.

Variation of catalyst amount is chosen as to find the optimize amount of catalyst that can be used in bioalcohol production with its corresponding yield. Besides, the yield of specific bioalcohol is to be calculated. This is to specify what types of bioalcohol that can be produced through the partial saponification process.

As for the variation amount of calcium methoxide that acted as base and catalyst, it is meant to observe if the calcium methoxide is to replace the base used, calcium hydroxide, will the calcium methoxide manage gain more yield than the usual method. If calcium methoxide can replace calcium hydroxide, it will contribute towards the sustainability in term of environment and economy as the number of chemical used is reduced. Thus, the production cost of bioalcohol can be reduced as well.

5.2 QUALITATIVE AND QUANTITATIVE ANALYSIS

The qualitative and quantitative analysis is meant to analyze the amount of bioalcohol produced and its corresponding concentration. Thus, the yield of specific bioalcohol, mainly biomethanol and bioethanol can be calculated.

5.2.1 Gas Chromatography

The gas chromatography (GC) is a chromatographic technique that can be used to separate organic compounds that are volatile. A gas chromatograph consists of flowing mobile phase, an injection port, a separation column containing the stationary phase, a detector and a data recording system. From the sample injected, which in this case is the bioalcohol product gained; the organic compounds are separated due to differences in their partitioning behaviour between the mobile gas phase and the stationary phase in the column. Details of the procedure will be discussed in Chapter 7.

CHAPTER 6
UTP CURRENT RESEARCH

In Universiti Teknologi PETRONAS (UTP), research in biofuel has been developed for more than two years. UTP has given considerable efforts in finding the best method for bioalcohol and biodiesel production, besides improving the performance of the hydrocarbon based diesel fuels. Studies were done towards various raw materials, catalysts and processes.

6.1 NOVEL ROUTE OF BIOFUEL PRODUCTION (BIOMETHANOL AND BIODIESEL) FROM COCONUT AND MAIZE

This research was done by J.H. Hayati (2007), and is meant to produce biofuel through the integration of biomethanol and biodiesel production. This project is focusing on using biomethanol as bioalcohol and coconut and maize as the raw materials. The project works involved are saponification and transesterification processes.

By comparing coconut oil yield and maize oil yield, the results show that the percentage of oil contained in coconut oil is higher than the oil contained in maize. In 20kg of sample, maize can produce 0.44g of oil and coconut can produce 12.4g of oil. However, the yield percentage of oil contents for maize and coconut are more than 100% due to the impurities which have not been successfully removed by the absorbent.

Biomethanol was being produced by using two methods – conventional and in-situ saponification. Both methods were compared, and the results show that conventional metjod produces more biomethanol but in-situ saponification seems to be more reliable as the results gained are similar to the theory results. In conclusion, both methods can be used to produce biomethanol.

For biodiesel production, again, it is being produced by using two methods – conventional and in-situ transesterification. Both results gained were compared, and it shows that conventional method produced more biodiesel. However, in-situ transesterification processing steps have been reduced, and it is more time-effective.

The last experiment is to produce biodiesel by varying the reaction time, volume of base $Ca(OH)_2$, and percentage of catalyst (KOH). By varying the reaction time, results showed that the reaction time that produced high percentage of biodiesel is 2 hours. Furthermore, by varying the volume of base, results showed that 40 ml of $Ca(OH)_2$ is preferred to obtain high percentage of biodiesel. Also, 1 weight percent (wt%) of KOH as catalyst is the minimum value that can provide enough activation energy for the biodiesel process.

Source: (Hayati, 2007)

6.2 METHANOL SYNTHESIS FROM NATURAL SOURCES

This project is carried out by A. R. Arifin Azahari (2007), and the main objective of this project is to produce methanol from coconut oil and to find the optimum experimental conditions for the best yield of biomethanol. In addition, the effect of blending methanol with gasoline on viscosity performance is studied.

The first study is to observe the quantity of oil produced from coconut, with changes in extraction time. The results showed that as the extraction time increases, the yield of coconut oil increases.

The optimum conditions for methanol synthesis was found at temperature 40°C, with feed ratio 5:1 (200 ml of extracted oil to 40 ml of $Ca(OH)_2$) and reaction time 60 minutes. The optimum yield of methanol synthesis is around 2.4% only.

From the kinematic viscosity determination experiment, the viscosity increases as the amount of biomethanol increases. However, there are a few errors in the results value. This may be due to the mixture methanol-gasoline that is not well mixed.

Source: (Azahari, 2007)

6.3 EFFECTS OF EXPERIMENTAL SETUP ON BIOALCOHOL PRODUCTION FROM PALM KERNEL OIL (PKO)

This project is done by A. Ina Czarina (2007), and is meant to investigate the effect of different of experimental setup on bioalcohol production from PKO and to find best experimental setup which can produce bioalcohol at lab scale. Four methods of bioalcohol production were analyzed, namely: Method I: Reaction using water bath, Method II: Reaction using ultrasonic bath, Method III: Reaction using hot plate and magnetic stirrer (with and without condenser) and Method IV: Reaction with direct heating method.

The results showed that bioalcohol can only be produced in Method II, III and IV. Method I is not feasible at all. Method II (ultrasonic bath) yields bioalcohol but with low concentration of biomethanol (0.0042M and 0.0035M) and bioethanol (0.0022M and 0.0017M). The second feasible method is Method III (hot plate with condenser) which yields around 0.0009M of biomethanol and 0.0001M of bioethanol.

Method I was unable to produce any bioalcohol. This was due to the saponification reaction, whereby the PKO needed to be heated up first to 60°C prior to mixing with $Ca(OH)_2$ to ensure enough heat of reaction. As to avoid the bioalcohol produced during reaction from escaping to the atmosphere, the conical flask used in the reaction should be plugged with a stopper or any other means. Additionally, because of the characteristic of PKO that easily to be solidified, the reacted product cannot be kept overnight. This is because, if the product solidified, it will need to be heated up again and might cause the product to undergo further reaction to produce soap and glycerol. In addition, the reacted product should be cooled down to 40°C (before the product solidified) after 2 hours of reaction at 60°C prior to further separation in the rotary evaporator. This is to avoid the produced bioalcohol (which might still be in vapour form) to escape to the atmosphere.

As for Method IV, direct heating only produced a very small amount of bioalcohol. There was also inconsistency of bioalcohol produced. This was due to method, whereby direct heating had less heat distribution. Hence, the bottom part will receives more heat and tendency for the heat to dissipate to the whole mixture is low, due to the fact that there might be dissipation to the surrounding as well. Thus, the activation energy could not be reached and reaction kinetic was not achieved. Source: (Czarina, 2007)

6.4 EFFECT OF CATALYST ADDITION IN BIOALCOHOL PRODUCTION FROM PALM KERNEL OIL

This project is done by A. S. Shahidah (2008), and the aim of this project is to observe the effect of catalyst addition in bioalcohol production. The catalysts used are sodium methoxide and sodium ethoxide. This project is carried out by using partial saponification.

The results showed that the bioalcohol production increases when catalyst, NaOMe is used. Besides, as the weight percent of catalyst increases, the amount of bioalcohol produced increases. However, it is only applied for 0.3 and 0.5wt% of NaOMe. For 0.7, 1.0 and 2.0wt% of NaOMe, the reaction produces soap instead of bioalcohol. This may be due because of the side reactions occurred.

As for the sodium ethoxide (NaOEt), the ethanol production increased significantly. This showed that the reaction was to be auto-catalytic. From both experiments, the average yield of biomethanol is approximately 30% with an addition of 0.5wt% of NaOMe, while the average yield of bioethanol is about 285% with an addition of 1.0wt% of NaOEt. There might be some errors on the experiment or the calculations since the yield exceed 100%.

Source: (Shahidah, 2008)

CHAPTER 7
METHODOLOGY

This chapter will discuss the experimental procedure including the equipments and chemicals used. The experiments can be divided into 3 subsections as shown in Table 7 below:

Table 7: Experimental works summary

Experiment No.	Title of Experiment	Overview
Experiment 1	Bioalcohol production without catalyst.	A saponification reaction between PKO and $Ca(OH)_2$ as base to produce bioalcohol.
Experiment 2	Bioalcohol production with presence of catalyst.	A saponification reaction between PKO and $Ca(OH)_2$ as base, with presence of catalyst to produce bioalcohol. Catalyst used is sodium methoxide, NaOMe Manipulated variable is the amount of catalyst – 0.05, 0.1, 0.3 and 0.5wt% catalyst by weight of oil.
Experiment 3	Bioalcohol production by using calcium methoxide.	A saponification reaction between PKO and calcium methoxide as base and catalyst to produce bioalcohol. Manipulated variable is the amount of calcium methoxide – 0.05, 0.1, 0.5, 1.0 and 2.0wt% by weight of oil.

7.1 EXPERIMENTAL METHODOLOGY

7.1.1 Experiment 1: Bioalcohol Production without Catalyst

In this experiment, bioalcohol will be produced by using saponification method without the presence of catalyst. The apparatus and experimental conditions will be based on the findings by A. Ina Czarina (2008). The parameters used for all experimental setup are based on the optimum condition obtained from the previous research on bioalcohol production using reactor by H. Azlinda et al. (2007). The parameters are:

Temperature	: 60^0C
Pressure	: 1 atm
Base	: 0.05M Calcium Hydroxide, $Ca(OH)_2$
Reaction Time	: 2 hours
Feed ratio (PKO:base)	: 5:1

This experiment is repeated for three times to ensure reproducibility of the results. Below are the details of experiment:

Objective: To produce bioalcohol without the presence of catalyst

Materials/Chemicals:

- 200ml PKO
- 40ml 0.05M $Ca(OH)_2$

Equipments/Apparatus:

- Round bottom flask with two openings
- Hot plate and magnetic stirrer
- Condenser
- Rotary evaporator

Procedures:

A. Preparation of base 0.05M calcium hydroxide, $Ca(OH)_2$.

0.05M of $Ca(OH)_2$ solution is prepared by weighing 1.85g of solid $Ca(OH)_2$ and diluted it in a 500ml volumetric flask of distilled water.

B. Preparation of alcohol standard for Gas Chromatography purposes.

The alcohol standard for methanol, ethanol, propanol and butanol with 0.1M, 0.01M and 0.001M each are prepared in a 50ml volumetric flask of distilled water.

C. Bioalcohol production through a saponification method without presence of catalyst.

1. 200ml of PKO is placed in a round bottom flask with two openings.

2. The flask is submerged into a container of water, which will be placed on top of a hot plate. Then, the oil is heated up until it reaches 60^0C.

   Note: Submerging the flask into a container of water is meant to en sure uniform heat distribution. A. Ina Czarina (2008) has found out that the PKO need to be heated up first to 60^0C prior to mixing with $Ca(OH)_2$ to ensure enough heat for reaction.

3. When the temperature of oil reaches 60^0C, 40ml of 0.05M $Ca(OH)_2$ is added. The mixture is mixed by using a magnetic stirrer for 2 hours to ensure uniform mixing. the mixing rate is set to 300 – 400 rpm.

   Caution: The reaction needs to be maintained approximately 60^0C throughout the entire process to avoid overheating or insufficient heat for reaction.

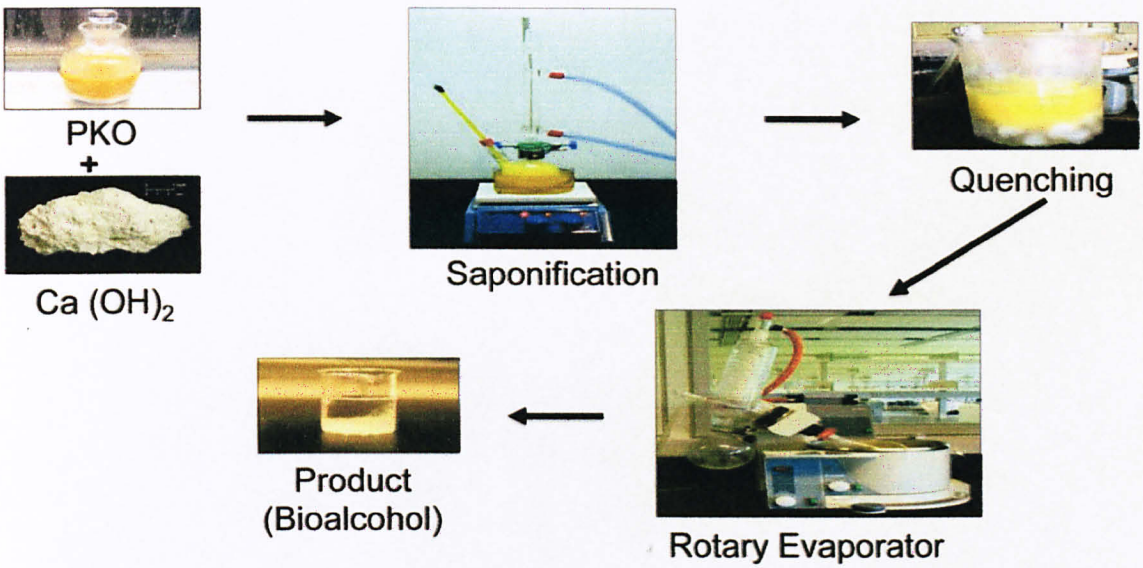
4. After 2 hours of reaction, the reacted product is quenched for approximately 5 minutes to avoid any bioalcohols from vaporizing. Next, the reacted product is distillate using rotary evaporator for 1 hour at 90^0C.

Note: At 90^0C, it is believed that all possible bioalcohols – methanol and ethanol are expected to vaporize and purified from the solvent, since these alcohols have boiling point below 90^0C.

5. The distillate product is collected from the collector of rotary evaporator and it is cooled down to room temperature prior to analyze using Gas Chromatography (GC).

6. The experiment is repeated from step 1 – 6 with two other samples.

7. The products are analyzed using GC.



7.1.2 Experiment 2: Bioalcohol Production with Presence of Catalyst, NaOMe

In this experiment, the catalyst used is sodium methoxide, NaOMe. The manipulating variable is the amount of catalyst, varies from 0.05, 0.1, 0.3 and 0.5wt% by weight of oil. Each experiment is repeated for three times to ensure reproducibility of the results. Details of the experiment are as below:

Objective: To study the effect of varies amount of catalyst on bioalcohol production.

Materials/Chemicals:

- 200ml PKO
- 40ml 0.05M $Ca(OH)_2$
- $NaOCH_3$

Equipments/Apparatus:

- Round bottom flask with two openings
- Hot plate and magnetic stirrer
- Condenser
- Rotary evaporator

Procedures:

Procedures for this experiment will be the same as in section 7.1.1 – Bioalcohol production without catalyst. However, in step 3, catalyst NaOMe need to be added together with $Ca(OH)_2$.

The first experiment used 0.05wt% of catalyst NaOMe and it is repeated for two times. The experiment is then repeated by varying the amount of NaOMe from 0.1, 0.3 and 0.5wt% by weight of oil.

7.1.3 Experiment 3: Bioalcohol Production by Using Calcium Methoxide as Base and Catalyst

In this experiment, calcium methoxide CaOMe is used as base and at the same time as catalyst. The feed ratio of PKO:Base is 5:1. It means that the CaOMe amount that is needed to react with 200ml of PKO must be at least 40ml as to meet the requirement of PKO:base ratio of 5:1.

The manipulating variable is the amount of CaOMe, varies from 0.1, 0.5 and 1.0 and 2.0wt% by weight of oil. This additional CaOMe will be added together with 40ml CaOMe. Each experiment is repeated for two times to ensure reproducibility of the results. Details of the experiment are as below:

Objective: To study the effect of varies amount of calcium methoxide as base and catalyst on bioalcohol production.

Materials/Chemicals:

- 200ml PKO
- 0.05M $CaOCH_3$

Equipments/Apparatus:

- Round bottom flask with two openings
- Hot plate and magnetic stirrer
- Condenser
- Rotary evaporator

Procedures:

A. Preparation of 0.05M calcium methoxide, CaOMe

0.05M CaOMe solution is prepared by adding 2.55g of solid CaOMe and dilute it in a 500ml volumetric flask of distilled water. CaOMe need to be heated approximately at 60°C while diluting it in distilled water.

B. Bioalcohol Production by Using Calcium Methoxide as Base and Catalyst

Procedures for this experiment will be the same as in section 7.1.1 – Bioalcohol production without catalyst. However, in step 3, CaOMe is to replace the $Ca(OH)_2$.

Thus, 40ml of CaOMe is added along with 0.05wt% of CaOMe by weight of oil.

Note: 40ml of CaOMe will act as base while 0.05wt% of CaOMe by weight of oil will act as catalyst.

The experiment is repeated for two times. The experiment is then repeated by varying the amount of CaOMe from 0.1, 0.3, 0.5 and 1.0wt% by weight of oil.

7.2 ANALYTICAL METHODOLOGY

7.2.1 Gas Chromatography

Objective: To quantify the amount of bioalcohol produced.

Procedures:

All the bioalcohol samples will be put into a small cylinder bottles. Then, the cylinder bottles are put on the GC to be analyzed. First, the sample bottles will be injected at the injection port using a syringe needle. Next, the components of the mixture will moved through the GC column. Difference in the component partitioning behaviour between the mobile phase and stationary phase cause the component to reach the detector at varying times. Then, the detector sends signal to the data recording system resulting a peak on the chart paper. A graph of detector response (y-axis) against retention time (x-axis) is generated. By observing the retention time, it helps to identify the samples if the method condition is constant.

The alcohol standards prepared is analyzed first using the GC. The data of the alcohol standard is saved on the computer so that when the bioalcohol samples are analyzed, the sample will be categorized based on the alcohol standards.

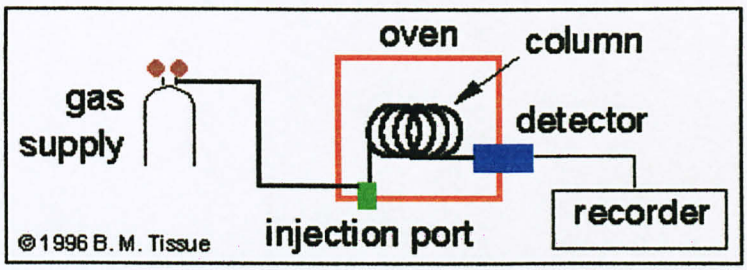


Figure 21: Schematic diagram of gas chromatography.

CHAPTER 8

RESULTS AND DISCUSSIONS

8.1 OVERVIEW

In this chapter, results of every experiment will be discussed. The first and second experiments - the bioalcohol production without and with catalyst NaOMe has been completely done. Experiment 3 which is the bioalcohol production by using calcium methoxide as base and catalyst is partially done.

The results and discussions for Experiment 1 and 2 are discussed below.

8.1 RETENTION TIME, t_R

From the calibration curve obtained from GC analysis, the retention time of methanol and ethanol are as below:

Table 8: Retention time of alcohol

Types of Alcohol	Retention Time, t_R (mins)
Methanol	2.2
Ethanol	2.4

8.2 EXPERIMENT 1: BIOALCOHOL PRODUCTION WITHOUT CATALYST

Results of experiment 1 are as in Table 9 below:

Table 9: Results of experiment 1 – bioalcohol production without catalyst

Sample	Volume (ml)	Concentration (M)	
		Methanol	Ethanol
1A	10	0.0000	0.0000
2A	6	0.0080	0.0072
3A	11	0.0000	0.0005
Average	**9**	**0.0027**	**0.0026**

From Table 3, the average of methanol concentration is about 0.0027M and the average of ethanol concentration is 0.0026M. The results could not be exactly verified since the significant amount of methanol can only be seen from sample 2A. Besides, there is a significant difference between the concentration of ethanol in sample 2A and 3A. Some errors might happen while carrying out this experiment that caused the inconsistency of results. The errors are:

- **Inconsistency of reaction temperature**

  These problems may be because of the inconsistency of reaction temperature. The reaction temperature needs to be maintained at 60^0C throughout the two hours of reaction. However, due to the hot plate temperature scale is in numbering 1 to 6, it is hard to determine the temperature and its respected number.

  A thermometer has been inserted into the flask to monitor the temperature. Still, any slightly increment and decline of temperature may take time for it to be maintained back to 60°C. The time lag to maintain the reaction temperature to 60°C has caused overheating or insufficient heat for reaction.

- **Overheating**

  As stated in the experimental procedure, overheating might causes the alcohol to be evaporated since methanol boiling point is about 65^0C. This explained the undetectable of methanol and small concentration of ethanol from the results.

In addition, propanol and butanol are not appeared in the GC results as the values are too small, and the GC has been set to show values up to four decimal points. Besides, due to the equipment failure of rotary evaporator that has a higher temperature range, the experiment can only be carried out by using a rotary evaporator that has a maximum temperature range of 90°C. As the temperature of the rotary evaporator is set to the maximum temperature of 90°C, a thermometer is put to the heating bath on the rotary evaporator. The exact maximum temperature of the rotary evaporator is only about 82°C. And this may be because the heat from the heater is released to the environment.

The boiling point of propanol is approximately 97^0C and butanol is 118^0C. Therefore, it is believed that not all propanol and butanol are evaporated during distillation of reacted product by using rotary evaporator.

8.3 EXPERIMENT 2: BIOALCOHOL PRODUCTION WITH PRESENCE OF CATALYST, NaOMe

In this experiment, only 0.05 and 0.1wt% of NaOMe by weight of oil yield bioalcohol, while 0.3 and 0.5wt% of NaOMe yield soap instead of bioalcohol. This will be discussed later in this section.

Results for 0.05wt% of NaOMe by weight of oil are as below:

Table 10: Results of bioalcohol production with presence of catalyst NaOMe 0.05wt% by weight of oil.

Sample	Mass (g)	Volume (ml)	Concentration (M)	
			Methanol	Ethanol
1B	53.87	49.33	0.0616	0.0000
2B	52.58	48.00	0.0637	0.0043
3B	52.91	46.50	0.1660	0.0039
Average	**53.12**	**47.94**	**0.0971**	**0.0027**

Results for 0.1wt% of NaOMe by weight of oil are as below:

Table 11: Results of bioalcohol production with presence of catalyst NaOMe 0.1wt% by weight of oil.

Sample	Mass (g)	Volume (ml)	Concentration (M)	
			Methanol	Ethanol
1C	53.75	46.67	0.0847	0.0000
2C	55.01	50.67	0.0966	0.0047
3C	56.83	49.50	0.1927	0.0038
Average	**55.20**	**48.94**	**0.1247**	**0.0028**

From Table 10 and 11, the average concentration of methanol for 0.05wt% of NaOMe by weight of oil is lower compared to the 0.1wt% of NaOMe by weight of oil. The average concentration of methanol for 0.05wt% NaOMe is 0.0971M and 0.1wt% NaOMe is 0.1247M. The same goes to the ethanol concentration. The average concentration of ethanol for 0.05wt% NaOMe is 0.0006M and 0.1wt% NaOMe is 0.0015M. Hence, it can be said that as the amount of catalyst increases, the concentration of bioalcohol produced also increases.

However, for the 0.3 and 0.5wt% of NaOMe by weight of oil, there has not been any result generated since the saponification reaction has produced soap. After the two hours reaction, there are two layers of reacted products that can be seen. The bottom part's colour is light yellow and the upper part's colour is dark yellow. The reacted products seem not to be uniformly mixed.

As the mixture is send to the rotary evaporator for distillation process, the mixture in evaporation flask boiled while it is being distillate. The mixture started to boil at temperature 60^0C and form bubbles. All mixture in the evaporation flask goes directly to the collection flask, leaving neither liquid nor solid residual in the evaporation flask. This problem hindered the solution to be distilled using rotary evaporator. Provided that the boiling point for methanol and ethanol are 65^0C and 78^0C respectively, it is assumed that there is no methanol and ethanol in the reacted products.

For experiment 2, it can be concluded that as the amount of catalyst increases, the yield and concentration of bioalcohol increase. However, excessive amount of catalyst may results in high yield of soap and less yield of ester, causing the reacted products to produce soap rather than bioalcohol. Thus, the optimum amount of catalyst sodium methoxide is 0.1wt% by weight of oil.

8.4 EXPERIMENT 3: BIOALCOHOL PRODUCTION BY USING CALCIUM METHOXIDE, CaOMe

8.4.1 Experimental Setup

On the early stage of this experiment, before proceeding to the final methodology of producing bioalcohol by using calcium methoxide, the experimental setup for this experiment is studied. Three methods are studied:

- **Method I**: Bioalcohol production by using calcium hydroxide $Ca(OH)_2$ is used as base, with presence of calcium methoxide CaOMe catalyst. The calcium methoxide is in solid form.
- **Method II**: Bioalcohol production by using calcium hydroxide $Ca(OH)_2$ is used as base, with presence of calcium methoxide CaOMe catalyst. The calcium methoxide is in liquid form (diluted in distilled water).
- **Method III**: Bioalcohol production by using calcium methoxide as base and catalyst at the same time. The calcium methoxide is in solid form.
- **Method IV**: Bioalcohol production by using calcium methoxide as base and catalyst at the same time. The calcium methoxide is in liquid form (diluted in distilled water).

Method I, II and IV can produce bioalcohol, but not method III. This is because the solid form of sodium methoxide did not dissolve in PKO during the reaction. Thus, it resulted in no distillate product during distillation by using rotary evaporator. It is believed that the two hours reaction is not enough for the fatty acids to react with calcium methoxide.

As to compare method II and IV, the concentration of bioalcohol production for method IV is higher as compared to method II. Besides, the volume of the bioalcohol produced from method IV is higher as compared to method II. At 1wt% of calcium methoxide by weight of oil, the results are as in Table 12 below:

Table 12: Results comparison between method II and method IV of bioalcohol production by using calcium methoxide.

Method	Average Concentration (M)		Average Volume (ml)
	Methanol	Ethanol	
Method II	0.0083	0.0099	12
Method IV	0.0215	0.0009	25

Since the methanol production is favoured over ethanol production, method IV is chosen to be the experimental setup for this experiment.

There is also other finding for the experimental setup. For method IV, at first, PKO and 0.1wt% of CaOMe are mixed together. However, no bioalcohol is generated while the mixtures are sent to the rotary evaporator for the distillation process. This may be because the amount of base which is the calcium is not enough. The requirement volume ratio of PKO to base should be 5:1. Thus, 0.1wt% of CaOMe which is equivalent to 0.181ml is not enough to react with PKO to produce bioalcohol.

Then, the experiment is changed. In order for the reaction to occur, 40ml of CaOMe is needed to react with 200ml of PKO. So, an experiment of reacting 200ml PKO with 40ml CaOMe is done. Bioalcohol managed to be produced. For the subsequent experiments, an additional of weight percent of CaOMe is added together with 40ml of CaOMe. For an example, for 0.1wt% of CaOMe by weight of oil, 40ml plus an additional of 0.18ml are added to react with PKO.

8.4.2 Experimental Results of Bioalcohol Production by Using Calcium Methoxide as Base and Catalyst

The experiment is carried out with variation amount of calcium methoxide: 0.0, 0.1, 0.5, 1.0 and 2.0wt% by weight of oil. All of these amounts managed to produce bioalcohol.

Results for no additional catalyst are as below:

Table 13: Results of bioalcohol production with CaOMe 0.0wt% by weight of oil.

Sample	Mass (g)	Volume (ml)	Concentration (M)	
			Methanol	Ethanol
1D	8.95	10.00	0.0219	0.0060
2D	12.72	14.00	0.0348	0.0018
Average	**10.84**	**12.00**	**0.0284**	**0.0004**
Std. Deviation		**2.83**		

Results for 0.1wt% of CaOMe by weight of oil are as below:

Table 14: Results of bioalcohol production with CaOMe 0.1wt% by weight of oil.

Sample	Mass (g)	Volume (ml)	Concentration (M)		
			Methanol	Ethanol	Propanol
1E	15.14	16.00	0.0287	0.0026	0.0009
2E	10.47	11.00	0.0402	0.0095	0.0008
Average	**12.81**	**13.50**	**0.0340**	**0.0061**	**0.0009**
Std. Deviation		**3.54**			

Results for 0.5wt% of CaOMe by weight of oil are as below:

Table 15: Results of bioalcohol production with CaOMe 0.5wt% by weight of oil.

Sample	Mass (g)	Volume (ml)	Concentration (M)	
			Methanol	Ethanol
1F	16.04	17.00	0.0401	0.0000
2F	13.86	15.00	0.0379	0.0000
Average	**14.95**	**16.00**	**0.0390**	**0.0000**
Std. Deviation		**1.41**		

Results for 1.0wt% of CaOMe by weight of oil are as below:

Table 16: Results of bioalcohol production with CaOMe 1.0wt% by weight of oil.

Sample	Mass (g)	Volume (ml)	Concentration (M)	
			Methanol	Ethanol
1G	20.55	25.00	0.0468	0.0014
2G	26.09	27.00	0.0366	0.0000
Average	**23.32**	**26.00**	**0.0417**	**0.0007**
Std. Deviation		**1.41**		

Results for 2.0wt% of CaOMe by weight of oil are as below:

Table 17: Results of bioalcohol production with CaOMe 2.0wt% by weight of oil.

Sample	Mass (g)	Volume (ml)	Concentration (M)	
			Methanol	Ethanol
1H	27.23	28.00	0.0495	0.0000
2H	25.99	27.00	0.0463	0.0000
Average	**26.61**	**27.50**	**0.0479**	**0.0000**
Std. Deviation		**0.71**		

From Table 13 until 17, the mass and volume of bioalcohol production increase as the amount of calcium methoxide increase. The same goes to the methanol concentration. Methanol concentration increases from 0.0284 to 0.0479M. Thus, the methanol concentration is proportional to the increment of calcium methoxide.

However, ethanol concentration seems unstable. The results for ethanol concentration at 0.1wt% of calcium methoxide is high, about 0.0061M. On the other hand, ethanol concentration at zero weight percent calcium methoxide and 1.0wt% is too low. Besides, at 0.5wt% and 2.0wt% of calcium methoxide, no ethanol is existed. Thus, it can be said that the optimize condition for ethanol production is at 0.1wt% of calcium methoxide.

The same goes to the propanol production. Propanol production can only be seen at 0.1wt% of calcium methoxide. Hence, it can also be said that the optimum condition of producing propanol is at this amount of calcium methoxide.

From the results, it can be concluded that the methanol will keep increasing as the amount of calcium methoxide increases. The optimize condition of producing the highest yield can only be determined if this project is to be extended, in such a way that experiments need to extend to higher amount of calcium methoxide. However, for ethanol and propanol production, the optimize condition is at 0.1wt% of calcium methoxide. As the amount of calcium methoxide exceed 0.1wt%, the production of these alcohols will depreciate.

8.5 AUTOCATALYTIC REACTION

Autocatalytic or autocatalysis is a term used when a single chemical reaction product itself is the catalyst or reactant for that reaction. It is believed that the experiments conducted have undergone an autocatalytic reaction.

For the first experiment, it can be seen from the base calcium hydroxide, $Ca(OH)_2$ which contains the OH^- group which is same as the bioalcohol produced, (CH_3OH and C_2H_5OH) which also contains the OH^- group.

For the second and third experiments whereby sodium methoxide and calcium methoxide are used, these two catalysts contain CH_3O^- group. The CH_3O^- group is the same as what contain in the bioalcohol produced.

The chemical equation for the second order autocatalytic reaction is:

$$A + B \rightleftharpoons 2B$$

and the rate equation can be written as below:

$$r = k[A][B]$$

From the chemical equation, molecule of species A reacts with molecule of species B. The A molecule is converted into B molecule. Thus, the final product consists of the original B molecule and the B molecule created in the reaction. In the bioalcohol production, the methanol and ethanol produced consist of the original OH^- group or CH_3O^- group from reactant and catalyst, and the OH^- group or CH_3O^- group created in the reaction.

8.6 INCREMENT OF BIOALCOHOL PRODUCTION

This section helps in determining the effectivity of the variation amount of catalyst towards the bioalcohol production. Two types of increment of bioalcohol production are observed:

- Increment of bioalcohol concentration
- Increment of bioalcohol volume

All experiments done are taken into consider in observing the increment of bioalcohol production.

8.6.1 Increment of Bioalcohol Concentration

Summary of increment of bioalcohol concentration is as below:

Table 18: Summary of bioalcohol concentration rise for catalyst sodium methoxide.

Experiment	Average Concentration Biomethanol (M)	Increment Percentage (%)	Average Concentration Bioethanol (M)	Increment Percentage (%)
No catalyst	0.0027	-	0.0026	-
0.05wt% NaOMe	0.0971	53.40	0.0027	-
0.1wt% NaOMe	0.1247	167.60	0.0028	-

Table 19: Summary of bioalcohol concentration rise for calcium methoxide.

Experiment	Average Concentration Biomethanol (M)	Increment Percentage (%)	Average Concentration Bioethanol (M)	Increment Percentage (%)
No catalyst	0.0284	71.82	0.0039	-
0.1wt% CaOMe	0.0345	108.79	0.0061	-
0.5wt% CaOMe	0.0390	136.36	0.0000	-
1wt% CaOMe	0.0417	152.73	0.0007	-
2wt% CaOMe	0.0479	190.30	0.0000	-

For biomethanol concentration rise of catalyst sodium methoxide, the difference is significance as compared to the bioethanol concentration rise. This is because of the methoxide ion CH_3O^- from the sodium methoxide catalyst that helps to exhibits more biomethanol instead of bioethanol, resulting in slow increment of bioethanol concentration. This shows that, until 0.1wt% NaOMe by weight of oil, the bioalcohol concentration produced is proportional to the catalyst amount. This can be clearly seen by referring to Figure 22 and 23 below.

As for the calcium methoxide situation, the concentration of biomethanol increases slowly as compared to sodium methoxide situation. This may be because of the methoxide ion is used for reaction with PKO rather than to exhibit the production of bioalcohol. In contrary, the bioethanol concentration is increases only up to 0.1wt% of CaOMe. At above 0.1wt%, bioethanol concentration starts to decline.

The increment percentage is computed by comparing the value with the value gained from the product of bioalcohol, by reacting the catalyst with the base. Since the reaction is autocatalytic reaction, there is tendency for the methoxide ion to be converted to product. Thus, the increment is needed as to determine the pure bioalcohol produced from the reaction.

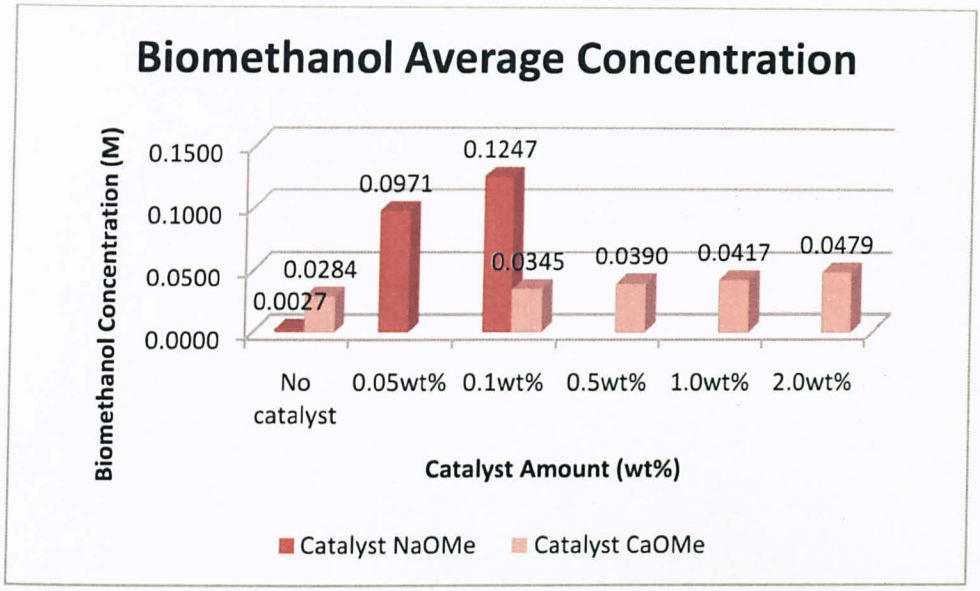


Figure 22: Biomethanol average concentration versus catalyst amount

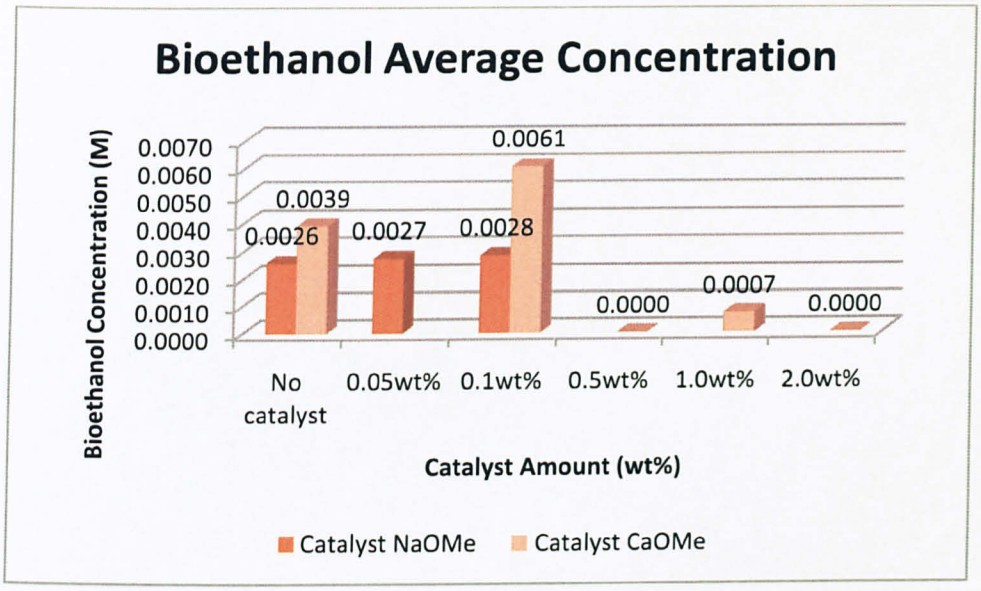


Figure 23: Bioethanol average concentration versus catalyst amount

8.6.2 Increment of Bioalcohol Volume

As for the volume of the bioalcohol produced, the results are as below:

Table 19: Summary of bioalcohol volume rise for catalyst sodium methoxide.

Experiment	Average Volume Biomethanol (M)	Increment Percentage (%)	Average Volume Bioethanol (M)	Increment Percentage (%)
No catalyst	4.5860	-	4.4140	-
0.05wt% NaOMe	46.6318	288.60	1.3127	-
0.1wt% NaOMe	47.8568	219.05	1.0877	-

Table 20: Summary of bioalcohol volume rise for calcium methoxide.

Experiment	Average Volume Biomethanol (M)	Increment Percentage (%)	Average Volume Bioethanol (M)	Increment Percentage (%)
No catalyst	10.5488	110.98	1.4512	-
0.1wt% CaOMe	11.4833	129.67	2.0167	-
0.5wt% CaOMe	16.0000	220.00	0.0000	-
1wt% CaOMe	25.5708	411.42	0.4292	-
2wt% CaOMe	27.5000	450.00	0.0000	-

For sodium methoxide, the average volume of biomethanol increases proportionally to the increment of catalyst added while the average volume of bioethanol decreases as the catalyst amount increases. This is also because of the methoxide ion from the sodium methoxide that helps to exhibit more biomethanol compared to bioethanol. Thus, resulting in increment of biomethanol volume and decline in bioethanol volume. This can be clearly seen from Figure 24 and 25 below.

As for the calcium methoxide, the average volume of biomethanol increases proportionally to the increment of catalyst added while the average volume of bioethanol

increases only up to 0.1wt% of calcium methoxide, and started to depreciate above 0.1wt% of calcium methoxide. Same as sodium methoxide, the methoxide ion helps to exhibit more biomethanol as compared to bioethanol. Thus, resulting in higher volume of biomethanol.

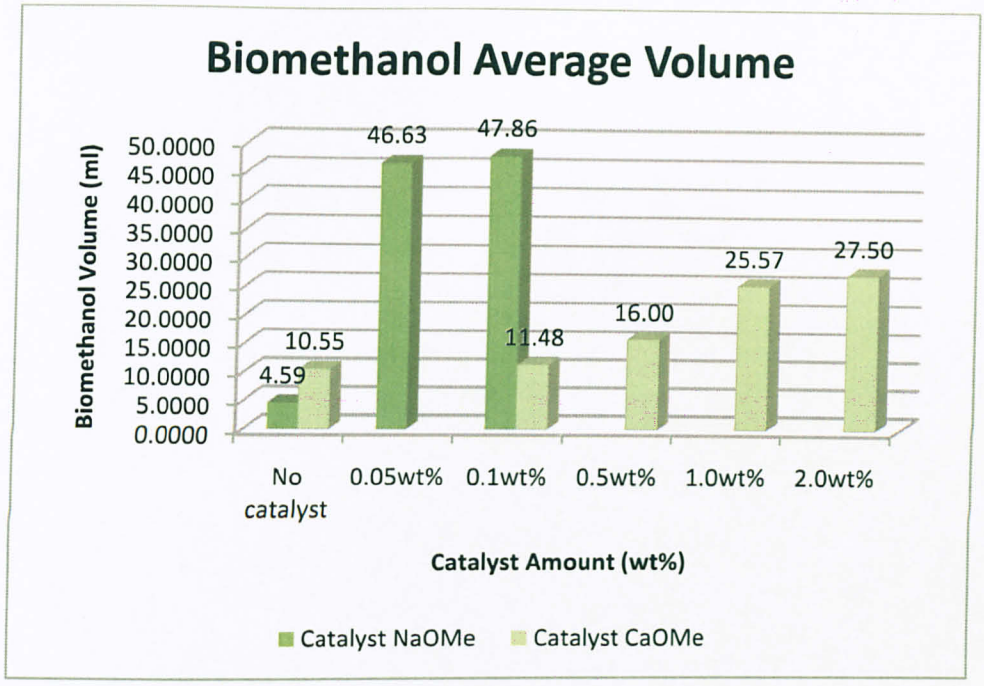


Figure 24: Biomethanol average volume versus catalyst amount.

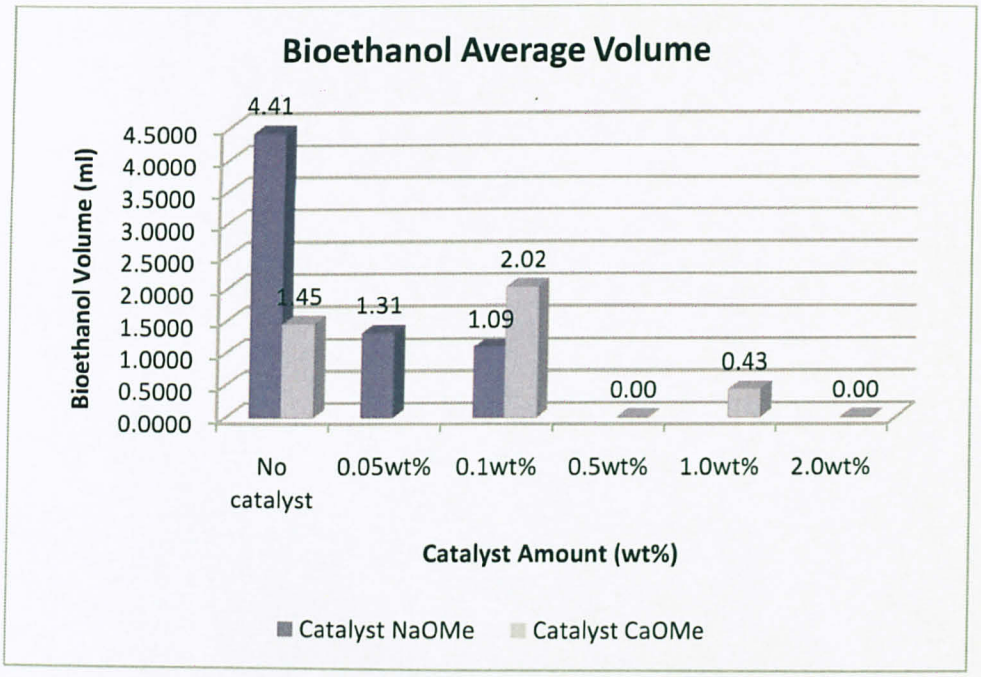


Figure 25: Bioethanol average volume versus catalyst amount.

Note: The calculations of average volume of bioalcohol is attached in Appendix I.

8.7 YIELD OF BIOALCOHOL

The yield of bioalcohol production is calculated based on the theoretical and actual mass. The calculations can be viewed through Appendix II and III. The results are as below.

From Figure 26 and 27, the yield of biomethanol increases proportionally to the increment of catalyst sodium methoxide amount while the yield of bioethanol decreases as the catalyst amount increases. For catalyst sodium methoxide, the yield of biomethanol increases up to 12% with 0.1wt% of catalyst. However, the yield of bioethanol decreases from 0.0173% with no catalyst to 0.0098% with 0.1wt% catalyst. On the other hand, for calcium methoxide, the yield of biomethanol increases up to 2.64% from 0.63% when there is no catalyst. The increment is only about 2%. For the bioethanol yield, the yield is optimized only at 0.1wt% of CaOMe.

The reason for this matter is the same as discussed in the previous section. This is cause by the methoxide ion from the sodium methoxide that will exhibits more biomethanol compared to the bioethanol. Besides, due to the low polarity between sodium methoxide and biomethanol, the biomethanol yield more than bioethanol.

The yield of bioethanol can be increases if sodium ethoxide is used as catasyt, as the ethoxide ion will exhibits more bioethanol compared to the biomethanol.

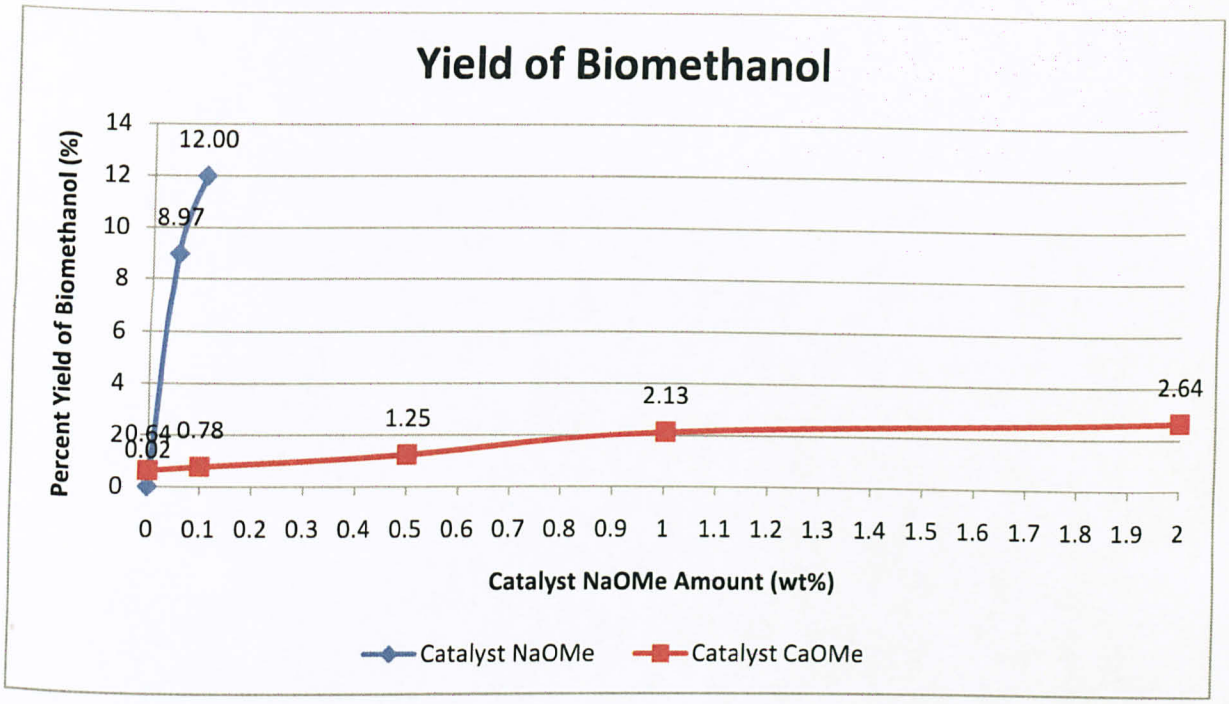


Figure 26: Average yield of biomethanol versus catalyst amount.

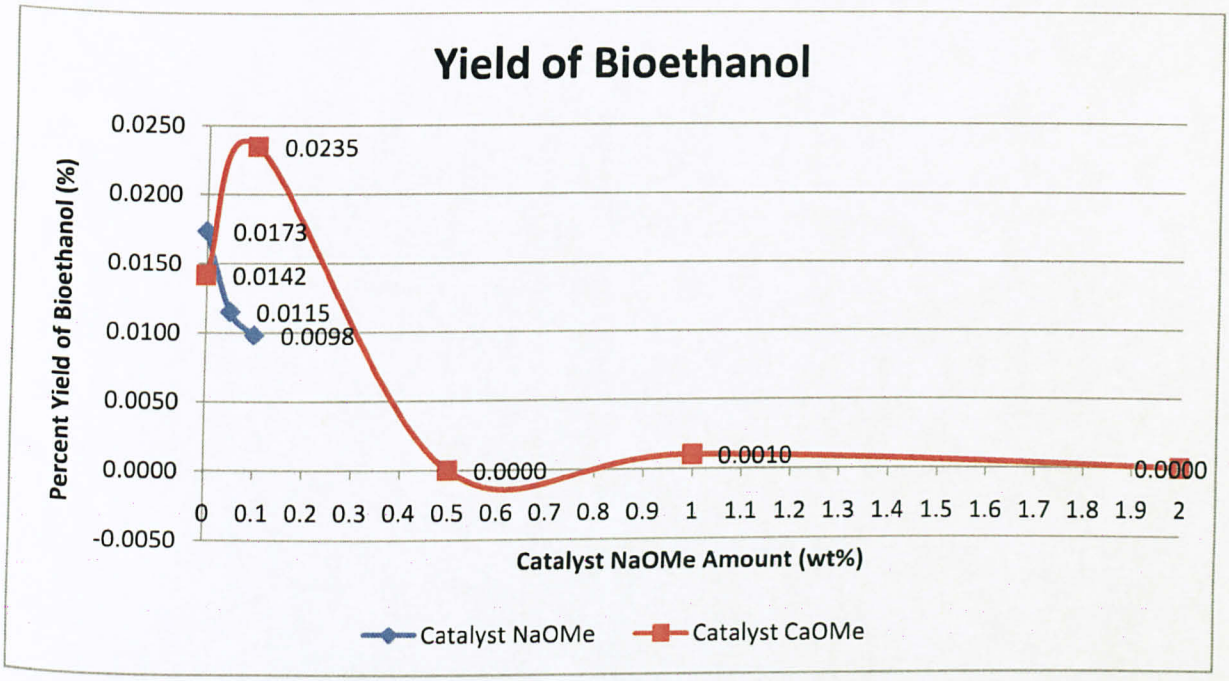


Figure 27: Average yield of bioethanol versus catalyst amount.

8.8 BIOALCOHOL PRODUCTION FROM CATALYST

8.8.1 Sodium Methoxide

This section is meant to determine the bioalcohol that can be produced from sodium methoxide. This is because of the auto catalytic reaction whereby the product of the reaction is the catalyst itself. This is applied to Experiment 2. The chemical reaction equation is as below:

$$NaOCH_3 + Ca(OH)_2 \rightarrow CH_3OH + NaOH + CaO$$

In order to calculate the methanol produced from the above reaction, the limiting reactant need to be identified.

Table 21: Determination of the limiting reactant of reaction between sodium methoxide and calcium hydroxide.

	$NaOCH_3$	$Ca(OH)_2$
V (ml)	0.095	40
m (g)	0.09	1.85
MW	54	74.09
n (moles) = m/MW	0.002	0.025
	Limiting reactant!!	

From Table 21, sodium methoxide is the limiting reactant of this reaction. Thus, the amount and concentration of methanol produced from this reaction can be determined. The summary is as below:

Table 22: Summary of sodium methoxide consumed and methanol produced.

NaOMe consumed				MeOH should be produced			
wt%	Mass (g)	Volume (ml)	No. of Moles	No. of Moles	Mass (g)	Volume (ml)	Molarity (M)
0.05	0.09	0.095	0.002	0.002	0.053	0.067	0.002
0.1	0.18	0.190	0.003	0.003	0.107	0.135	0.003

From Table 22, addition of sodium methoxide will only contribute in changes of the amount of methanol produced and the methanol concentration. The mass and volume of methanol produced increases as the amount of sodium methoxide increases. The same goes to the concentration of methanol produced. The concentration is increases from 0.002M to 0.003M.

Note: The calculation of sodium methoxide consumed is attached in Appendix IV.

8.8.2 Calcium Methoxide

This section is meant to determine the bioalcohol that can be produced from calcium methoxide. This is because of the auto catalytic reaction whereby the product of the reaction is the catalyst itself. This is applied to Experiment 3. Hydrolysis of calcium methoxide is applied in this case. The chemical reaction equation is as below:

$$Ca(OCH_3)_2 + H_2O \rightarrow CH_3OH + Ca(OH)(OCH_3)$$

Table 23: Determination of the limiting reactant of reaction between calcium methoxide and water.

	$NaOCH_3$	H_2O
V (ml)	0.181	500
m (g)	0.18	500 000
MW	102.15	18
n (moles) = m/MW	0.0018	27 777.78
	Limiting reactant!!	

From Table 23, calcium methoxide is the limiting reactant of this reaction. Thus, the amount and concentration of methanol produced from this reaction can be determined. The summary is as below:

Table 24: Summary of calcium methoxide consumed and methanol produced.

CaOMe consumed				MeOH should be produced			
wt%	**Mass (g)**	**Volume (ml)**	**No. of Moles**	**No. of Moles**	**Mass (g)**	**Volume (ml)**	**Molarity (M)**
0.1	0.18	0.181	0.002	0.002	0.056	0.071	0.002
0.5	0.9	0.906	0.009	0.009	0.282	0.356	0.009
1	1.8	1.813	0.018	0.018	0.564	0.712	0.018
2	3.6	3.625	0.035	0.035	1.128	1.424	0.035

From Table 24, addition of calcium methoxide will only contribute in changes of the amount of methanol produced and the methanol concentration. The mass and volume of methanol produced increases as the amount of calcium methoxide increases. The same goes to the concentration of methanol produced. The concentration is increases from 0.002M to 0.035M.

Note: The calculation of calcium methoxide consumed is attached in Appendix V.

CHAPTER 9

CONCLUSION AND RECOMMENDATIONS

9.1 CONCLUSION

Partial saponification has the potential to produce alcohol in the form of bioalcohol. The components studied in this project are the effect of catalyst amount in the bioalcohol production and the effect of changing the base to calcium methoxide and besides act as a catalyst. From the results, for sodium methoxide experiments, yield of biomethanol is higher as compared to bioethanol. The biomethanol yield increases rapidly towards the increment of the catalyst amount. However, the optimize amount of sodium methoxide to be used is 0.1wt% by weight of oil. The reaction tends to form soap if excessive amount of sodium methoxide is inserted. As for the calcium methoxide experiment, the biomethanol increases as the amount of calcium methoxide increases. However, the increment is slow as compared to biomethanol production by using sodium methoxide. On the other hand, the bioethanol yield reach its optimize point at 0.1wt% of calcium methoxide. As overall, the production route of bioalcohol favours the production by using sodium methoxide as catalyst.

9.2 RECOMMENDATIONS

9.2.1 Varies the base concentration

This experiment can be enhanced by increasing the concentration of calcium methoxide. Effect of different concentration of calcium methoxide should be carried out to observe the yield of bioalcohol produced.

9.2.2 Other analysis method

Other analysis method can be done as to obtain more accurate and consistent results.

9.2.3 Use of high temperature range of rotary evaporator

High temperature range of rotary evaporator is needed as to see other production of bioalcohol such as propanol and butanol.

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APPENDICES

APPENDIX I

VOLUME OF BIOMETHANOL AND BIOETHANOL PRODUCED (EXPERIMENT 2)

	EXPERIMENT	Sample Concentration Methanol (M)			Average Concentration Methanol (M)	Sample Concentration Ethanol (M)			Average Concentration Ethanol (M)	Total Concentration MeOH + EtOH (M)
		1	2	3		1	2	3		
A	No catalyst	0.0000	0.0080	0.0000	**0.0027**	0.0000	0.0072	0.0005	**0.0026**	0.0052
B	0.05wt% NaOMe	0.0616	0.0637	0.1660	**0.0971**	0.0000	0.0043	0.0039	**0.0027**	0.0998
C	0.1wt% NaOMe	0.0847	0.0966	0.1927	**0.1247**	0.0000	0.0047	0.0038	**0.0028**	0.1275

Table continued:

	EXPERIMENT	Moles of Methanol	Moles of Ethanol	Average Total Volume of Product (ml)	Volume of Methanol (ml) V = no. of MeOH moles x Average Tot Volume	Volume of Ethanol (ml) V = no. of MeOH moles x Average Tot Volume
A	No catalyst	0.5096	0.4904	9.0000	4.5860	4.4140
B	0.05wt% NaOMe	0.9726	0.0274	47.9444	46.6318	1.3127
C	0.1wt% NaOMe	0.9778	0.0222	48.9444	47.8568	1.0877

VOLUME OF BIOMETHANOL AND BIOETHANOL PRODUCED (EXPERIMENT 3)

EXPERIMENT		Sample Concentration Methanol (M)		Average Concentration Methanol (M)	Sample Concentration Ethanol (M)		Average Concentration Ethanol (M)	Total Concentration MeOH + EtOH (M)
		1	2		1	2		
D	No catalyst	0.0219	0.0348	0.02835	0.006	0.0018	0.0039	0.03225
E	0.1wt% CaOMe	0.0287	0.0402	0.03445	0.0026	0.0095	0.00605	0.0405
F	0.5wt% CaOMe	0.0401	0.0379	0.039	0	0	0	0.039
G	1wt% CaOMe	0.0468	0.0366	0.0417	0.0014	0	0.0007	0.0424
H	2wt% CaOMe	0.0495	0.0463	0.0479	0	0	0	0.0479

Table continued:

EXPERIMENT		Moles of Methanol (assume = mol percent)	Moles of Ethanol (assume = mol percent)	Average Total Volume of Product (ml)	Volume of Methanol (ml) V = no. of MeOH moles x Average Tot Volume	Volume of Ethanol (ml) V = no. of MeOH moles x Average Tot Volume
D	No catalyst	0.8791	0.1209	12	10.5488	1.4512
E	0.1wt% CaOMe	0.8506	0.1494	13.5	11.4833	2.0167
F	0.5wt% CaOMe	1.0000	0.0000	16	16.0000	0.0000
G	1wt% CaOMe	0.9835	0.0165	26	25.5708	0.4292
H	2wt% CaOMe	1.0000	0.0000	27.5	27.5000	0.0000

APPENDIX II

YIELD OF METHANOL (EXPERIMENT 2)

1. Determination of Limiting Reactant

				2R'-COOR	+	Ca(OH)2	→	2R-OH **2CH3OH**	+	$(R'-COO)_2$ Ca
V (ml)				200		40				
m (g)				190		1.85				
MW				325.873		74.09				
n (moles) = m/MW			stoi = 2	0.5830	⇔	0.0250				
			if 1	0.2915						
						limiting reactant!!				

2. Theoretical Amount of Biomethanol

$$n = \frac{2 \text{ mol } CH3OH}{1 \text{ mol } Ca(OH)2} \times 0.0250$$

$$\mathbf{n = 0.0499}$$

$$n = \frac{\text{mass}}{\text{MW } CH3OH}$$

$$0.0499 = \frac{\text{mass}}{32}$$

$$\mathbf{mass = 1.5981}$$

YIELD OF METHANOL (EXPERIMENT 3)

1. Determination of Limiting Reactant

				2R'-COOR	+	Ca(OH)2	→	2R-OH **2CH3OH**	+	$(R'-COO)_2$ Ca
V (ml)				200		40				
m (g)				190		1.85				
MW				325.873		74.09				
n (moles) = m/MW			stoi = 2	0.5830	⇔	0.0250				
			if 1	0.2915						
						limiting reactant!!				

2. Theoretical Amount of Biomethanol

$$n = \frac{2 \text{ mol } CH_3OH}{1 \text{ mol } Ca(OH)_2} \times 0.0250$$

n = 0.0499

$$n = \frac{\text{mass}}{\text{MW } CH_3OH}$$

$$0.0499 = \frac{\text{mass}}{32}$$

mass = 1.5981

3. Actual Amount of Biomethanol

EXPERIMENT		Sample Concentration Methanol (M)		Total Concentration MeOH + EtOH (M)		Moles of Methanol (assume = mol percent)		Sample Volume (ml)	
		1	2	1	2	1	2	1	2
D	No catalyst	0.0219	0.0348	0.0279	0.0366	0.784946	0.95082	10	14
E	0.1wt% CaOMe	0.0287	0.0402	0.0313	0.0497	0.916933	0.808853	16	11
F	0.5wt% CaOMe	0.0401	0.0379	0.0401	0.0379	1	1	17	15
G	1wt% CaOMe	0.0468	0.0366	0.0482	0.0366	0.970954	1	25	27
H	2wt% CaOMe	0.0495	0.0463	0.0495	0.0463	1	1	28	27

Table continued:

EXPERIMENT		Volume of Methanol (ml)		Actual Amount of Methanol (g) = Molarity x Volume*MW/1000		Yield (%) =Actual Mass Methanol/ Theory Mass Methanol *100%		Average Yield of Methanol (%)	Std. Deviation
		1	2	1	2	1	2		
D	No catalyst	7.849462	13.31148	0.005501	0.014824	0.344225	0.927605	0.635915041	2.828427125
E	0.1wt% CaOMe	14.67093	8.897384	0.013474	0.011446	0.843135	0.71622	0.779677545	3.535533906
F	0.5wt% CaOMe	17	15	0.021814	0.018192	1.365058	1.138383	1.251720514	1.414213562
G	1wt% CaOMe	24.27386	27	0.036353	0.031622	2.274796	1.978804	2.126800104	1.414213562
H	2wt% CaOMe	28	27	0.044352	0.040003	2.775371	2.503241	2.639306068	0.707106781

APPENDIX III

YIELD OF BIOETHANOL (Experiment 2)

1. Determination of Limiting Reactant

		2R'-COOR	+	Ca(OH)2	→	2R-OH 2C2H5OH	+	$(R'-COO)_2$ Ca
V (ml)		200		40				
m (g)		190		1.85				
MW		339.873		74.09				
n (moles) = m/MW	stoi = 2	0.5590	⟷	0.0250				
	if 1	0.2795						
				limiting reactant!!				

2. Theoretical Amount of Bioethanol

$$n = \frac{2 \text{ mol } C_2H_5OH}{1 \text{ mol } Ca(OH)_2} \times 0.0250$$

$$\mathbf{n = 0.0499}$$

$$n = \frac{\text{mass}}{\text{MW}_{C_2H_5OH}}$$

$$0.0499 = \frac{\text{mass}}{46}$$

$$\text{mass} = 2.2972$$

3. Actual Amount of Bioethanol

Experiment		Sample Concentration Ethanol (M)			Total Concentration MeOH + EtOH (M)			Moles of Ethanol (assume = mol percent)			Sample Volume (ml)		
		1	2	3	1	2	3	1	2	3	1	2	3
A	No catalyst	0.0000	0.0072	0.0005	0.0000	0.0152	0.0005	0.0000	0.4737	1.0000	10.00	6.00	11.00
B	0.05wt% NaOMe	0.0000	0.0043	0.0039	0.0616	0.0680	0.1699	0.0000	0.0632	0.0230	49.33	48.00	46.50
C	0.1wt% NaOMe	0.0000	0.0047	0.0038	0.0847	0.1013	0.1965	0.0000	0.0464	0.0193	46.67	50.67	49.50

Table continued:

Experiment		Volume of Ethanol (ml)			Actual Amount of Ethanol (g) = Molarity x Volume x MW/1000			Yield (%) =Actual Mass Ethanol/ Theory Mass Ethanol x 100%			Average Yield of Ethanol (%)
		1	2	3	1	2	3	1	2	3	
A	No catalyst	0	2.842105	11	0	0.000941	0.000253	0	0.040976	0.011013	0.0173
B	0.05wt% NaOMe	0	3.035294	1.067393	0	0.0006	0.00019149	0	0.026135	0.008336	0.0115
C	0.1wt% NaOMe	0	2.350773	0.957252	0	0.000508	0.000167328	0	0.022124	0.007284	0.0098

YIELD OF BIOETHANOL (Experiment 2)

1. Determination of Limiting Reactant

		2R'-COOR	+	Ca(OH)2	→	2R-OH 2C2H5OH	+	$(R'-COO)_2$ Ca
V (ml)		200		40				
m (g)		190		1.85				
MW		339.873		74.09				
n (moles) = m/MW	stoi = 2	0.5590	⇔	0.0250				
	if 1	0.2795						
				limiting reactant!!				

2. Theoretical Amount of Bioethanol

$$n = \frac{2 \text{ mol } C_2H_5OH}{1 \text{ mol } Ca(OH)_2} \times 0.0250$$

$$\mathbf{n = 0.0499}$$

$$n = \frac{\text{mass}}{\text{MW}}$$

$$0.0499 = \frac{\text{C2H5OH mass}}{46}$$

$$\text{mass} = 2.2972$$

3. Actual Amount of Bioethanol

EXPERIMENT		Sample Concentration Methanol (M)		Total Concentration MeOH + EtOH (M)		Moles of Methanol (assume = mol percent)		Sample Volume (ml)	
		1	2	1	2	1	2	1	2
D	No catalyst	0.006	0.0018	0.0279	0.0366	0.215054	0.04918	10	14
E	0.1wt% CaOMe	0.0026	0.0095	0.0313	0.0497	0.083067	0.191147	16	11
F	0.5wt% CaOMe	0	0	0.0401	0.0379	0	0	17	15
G	1wt% CaOMe	0.0014	0	0.0482	0.0366	0.029046	0	25	27
H	2wt% CaOMe	0	0	0.0495	0.0463	0	0	28	27

Table continued:

EXPERIMENT		Volume of Methanol (ml)		Actual Amount of Methanol (g) = Molarity x Volume*MW/1000		Yield (%) =Actual Mass Methanol/ Theory Mass Methanol *100%		Average Yield of Methanol (%)	Std. Deviation
		1	2	1	2	1	2		
D	No catalyst	2.150538	0.688525	0.000594	5.7E-05	0.025838	0.002482	0.01415977	2.828427125
E	0.1wt% CaOMe	1.329073	2.102616	0.000159	0.000919	0.00692	0.039998	0.023458937	3.535533906
F	0.5wt% CaOMe	0	0	0	0	0	0	0	1.414213562
G	1wt% CaOMe	0.726141	0	4.68E-05	0	0.002036	0	0.001017834	1.414213562
H	2wt% CaOMe	0	0	0	0	0	0	0	0.707106781

APPENDIX IV

SODIUM METHOXIDE CONSUMED

PKO			NaOMe			
Density (g/ml)	**Volume (ml)**	**Mass (g)**	**Weight %**	**Mass (g)**	**Density (g/ml)**	**Volume (ml)**
0.9	200	180	0.05	**0.09**	0.945	**0.095**
0.9	200	180	0.1	**0.18**	0.945	**0.190**

APPENDIX V

CALCIUM METHOXIDE CONSUMED

	PKO				CaOMe	
Density (g/ml)	Volume (ml)	Mass (g)	Weight %	Mass (g)	Density (g/ml)	Volume (ml)
0.9	200	180	0.1	**0.18**	0.993	**0.181**
0.9	200	180	0.5	**0.9**	0.993	**0.906**
0.9	200	180	1	**1.8**	0.993	**1.813**
0.9	200	180	2	**3.6**	0.993	**3.625**